Guide Safety of Hydrogen and Hydrogen Systems

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American Institute of Aeronautics and Astronautics

Approved

Abstract

This Guide presents information that designers, builders, and users of hydrogen systems can use to avoid or resolve hydrogen hazards. Guidelines are presented for system design, materials selection, operations, storage, and transportation. Pertinent research is summarized, and the data are presented in a quick-reference form. Further information can be found in the extensive bibliography.

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Contents

Forewo	ord	xv
Scope		xvii
Acrony	yms	xviii
Terms	and Definitions	xx
Trader	marks	xxv
1	Basic Hydrogen Safety Guidelines	1
1.1	Introduction	1
1.1.1	General	1
1.1.2	Hydrogen Usage	1
1.1.3	Applicable Standards	2
1.2	Applicable Documents	5
1.3	Personnel Training	5
1.3.1	Hydrogen Handling Training	5
1.3.2	Designer Training	5
1.3.3	Operator Certification	6
1.3.4	Hazard Communication Program	6
1.3.5	Annual Review	6
1.4	Inherent Safety Features	6
1.4.1	Hazard Management	6
1.4.2	Barriers	6
1.4.3	Safety Systems	6
1.4.4	Safe Interface	6
1.5	Controls	7
1.5.1	Warning Systems	7
1.5.2	Flow Controls	7
1.5.3	Safety Features	7
1.6	Fail-Safe Design	7
1.6.1	Certification	7
1.6.2	Fail-Safe Design	7
1.6.3	Redundant Features	7
1.7	Safety Assessment and Mishap Reporting	7
1.7.1	Safety Review	7
1.7.2	Operating Procedures	7
1.7.3	Hazard Analyses	7
1.7.4	Mishap Reporting	7

1.8	Waiver Provisions	8
2	Properties and Hazards of Hydrogen	9
2.1	General Properties	9
2.2	Ortho- and Para-Hydrogen	9
2.3	Thermophysical Properties	9
2.4	Health Hazard Properties	10
2.5	Characteristic Properties of GH ₂	10
2.5.1	Buoyancy	10
2.5.2	Diffusion Coefficient in Air	10
2.5.3	Joule-Thomson Expansion	11
2.6	Characteristic Properties of LH ₂	11
2.6.1	Boiling Point	
2.6.2	Ice Formation	11
2.6.3	Liquid Air Formation	11
2.6.4	Solidification of Contaminants	11
2.6.5	Continuous Evaporation	11
2.6.6	Buoyancy	12
2.6.7	Electric Charge Accumulation	12
2.7	Characteristic Properties of SLH ₂	12
2.7.1	Vapor Pressure	12
2.7.2	Volume Change	12
2.7.3	Thermal Stratification	12
2.7.4	Thermal Acoustic Oscillation	12
2.7.5	Aging	13
2.7.6	Electric Charge Buildup	13
2.7.7	Ortho- to Para-Hydrogen Conversion	13
2.7.8	Helium Solubility	13
2.8	Combustion-Related Properties	13
2.8.1	General	13
2.8.2	Lack of Flame Color	13
2.8.3	Flame Temperature in Air	13
2.8.4	Burning Velocity in NTP Air	14
2.8.5	Thermal Energy Radiated from Flame to Surroundings	14
2.8.6	Limiting Oxygen Index	14
2.8.7	Ignition	14
2.8.8	Quenching Gap in NTP Air	15

2.8.9	Flammability	15
2.9	Flame Propagation	17
2.9.1	General	17
2.9.2	Deflagration	17
2.9.3	Detonation	17
2.9.4	Deflagration-to-Detonation Transition	
2.9.5	Energy of Explosion	19
2.10	Hydrogen Hazards	19
2.10.1	General	19
2.10.2	Accidents Involving Hydrogen	19
2.10.3	Common Hydrogen Hazards	
3	Materials for Hydrogen Service	
3.1	Considerations for Materials Selection	25
3.1.1	General	25
3.1.2	General Materials	25
3.1.3	Metallic Materials	25
3.1.4	Nonmetallic Materials	26
3.1.5	Clad Materials	26
3.1.6	Gasket Materials	27
3.1.7	Welds	
3.1.8	Material Properties	27
3.1.9	Forbidden Materials	
3.1.10	Quality Control	27
3.2	Hydrogen Embrittlement	
3.2.1	General	28
3.2.2	Types of Embrittlement	28
3.2.3	Effect on Mechanical Properties.	28
3.2.4	Surface and Surface Films	28
3.2.5	Effect of Electrical Discharge Machining	29
3.2.6	Effect of Trapping Sites	29
3.2.7	Reducing the Effects of Hydrogen Embrittlement	29
3.3	Thermal Considerations in Material Selection	30
3.3.1	Low-Temperature Mechanical Properties	30
3.3.2	Low-Temperature Embrittlement	30
3.3.3	Thermal Contraction	31
4	Hydrogen Facilities	32

4.1	Safety Policy	32
4.1.1	General	32
4.1.2	Installation Pressure Systems Manager	32
4.1.3	Fire Protection	32
4.2	Safety Reviews	33
4.2.1	New Facilities	33
4.2.2	Existing Facility Modification or Rehabilitation	34
4.2.3	Safety Assessment Review	34
4.2.4	Operating Procedures	34
4.2.5	Training	34
4.2.6	Emergency Procedures	34
4.3	General Facility Guidelines	34
4.3.1	Electrical Considerations	34
4.3.2	Bonding and Grounding	36
4.3.3	Roadways and Area Surfaces	36
4.3.4	Transfer Piping	37
4.3.5	Elimination of Ignition Sources	37
4.3.6	Illumination	38
4.3.7	Testing	39
4.4	Buildings and Test Chambers	39
4.4.1	Buildings	39
4.4.2	Laboratory Setting, Test Chamber, Test Cell, Test Stand	39
4.4.3	Weather Shelter or Canopy	40
4.4.4	Electrical Equipment	40
4.4.5	Ventilation	40
4.5	Control Rooms	41
4.5.1	Structure	41
4.5.2	Piping Systems	41
4.5.3	Ventilation	41
4.5.4	Inert Gases	41
4.6	Location and QD Guidelines	42
4.6.1	General	42
4.6.2	Storage Type	42
4.6.3	Minimum Quantity Storage	42
4.6.4	Location and QD Standards for GH ₂	42
4.6.5	Location and QD Standards for Nonpropellant Use of LH ₂	43

4.6.6	Location and QD Guidelines for Propellant Use of LH ₂	44
4.6.7	Location and QD Guidelines for SLH ₂	44
4.6.8	Location and QD Guidelines for Piping and Other Hydrogen Systems	44
4.7	Exclusion Areas	44
4.7.1	General	44
4.7.2	Access Control	45
4.7.3	Placarding, Posting, and Labeling	45
4.8	Protection of Hydrogen Systems and Surroundings	46
4.8.1	Barricades	46
4.8.2	Liquid and Vapor Travel and Confinement	47
4.8.3	Shields and Impoundment Areas	47
4.9	Fire Protection	
4.9.1	General	48
4.9.2	Exposure Protection.	48
4.9.3	Deluge Systems	49
4.10	Documentation, Tagging, and Labeling of Storage Vessels, Piping, and Components	49
4.10.1	General	49
4.10.2	Documentation	49
4.10.3	Tagging	50
4.10.4	Labeling	
4.11	Instrumentation and Monitoring	50
4.11.1	Instrumentation	50
4.11.2	Hydrogen Detection	51
4.11.3	Fire Detection	
4.11.4	System Monitoring	52
4.12	Examination, Inspection, and Recertification	52
4.12.1	General	52
4.12.2	Examinations	52
4.12.3	Testing and Recertification	52
4.12.4	Records	53
4.12.5	Schedule	53
5	Hydrogen Storage Vessels, Piping, and Components	54
5.1	General Requirements	54
5.1.1	General	54
5.1.2	Special Considerations	54
5.1.3	GH ₂ Temperature Considerations	54

5.2	Storage Vessels	54
5.2.1	Fixed and Mobile Storage Systems for GH ₂	54
5.2.2	Fixed and Mobile Storage Systems for LH ₂	55
5.2.3	Fixed and Mobile Storage Systems for SLH ₂	56
5.2.4	Aerospace Pressure Vessels	58
5.2.5	Supports	58
5.3	Piping Systems	58
5.3.1	General	58
5.3.2	Supports	59
5.3.3	Piping for GH ₂	
5.3.4	Piping for LH ₂ and SLH ₂	60
5.3.5	Bending and Forming Piping	
5.3.6	Double Block and Bleed	61
5.4	Components	62
5.4.1	Joints in Piping and Tubing	62
5.4.2	Pipe Connections	63
5.4.3	Fittings	64
5.4.4	Flanges	64
5.4.5	Flexible Hoses	64
5.4.6	Expansion Joints	64
5.4.7	V-Band Couplings	65
5.4.8	Valves	65
5.4.9	Transfer Connections	66
5.4.10	Gaskets and O-Rings	67
5.5	Overpressure Protection of Storage Vessels and Piping Systems	68
5.5.1	General	68
5.5.2	Safety Valves	68
5.5.3	Rupture Disks	69
5.5.4	Supplemental Pressure Relief	70
5.5.5	Failure Modes	70
5.6	Hydrogen Vent and Flare Systems	70
5.6.1	General	70
5.6.2	Venting	71
5.6.3	Hydrogen Disposal by Burning	71
5.6.4	Hydrogen Disposal Into Exhaust Systems	72
5.6.5	Deflagration Venting	73

5.6.6	Explosion Prevention	73
5.7	Contamination	73
5.7.1	General	73
5.7.2	Filters	73
5.7.3	Interconnected Systems	73
5.8	Vacuum System	74
5.8.1	General	74
5.8.2	Hydrogen Vacuum Pumps	75
6	Hydrogen and Hydrogen Fire Detection	77
6.1	Hydrogen Detection	77
6.1.1	General	77
6.1.2	GH ₂ Detection Specifications.	78
6.1.3	Detection Technologies	78
6.1.4	Hydrogen Detector Installation and Use	79
6.2	Hydrogen Fire Detection Systems	80
6.2.1	Hydrogen Fire Detection	80
6.2.2	Hydrogen Fire Detection Technologies	80
6.2.3	Hydrogen Fire Detector Installation and Use	81
7	Operating Procedures	82
7.1	General Policy	82
7.1.1	Personnel	82
7.1.2	Standard Operating Procedures	82
7.1.3	Special Operating Procedures	82
7.1.4	Repairs, Alterations, and Cleaning	82
7.1.5	Modifications, Repairs, or Decommissioning	83
7.1.6	Contamination Control	83
7.1.7	Hazards of Substituting Dewars	84
7.1.8	Protective Clothing	85
7.2	Storage and Transfer Procedures	85
7.2.1	LH ₂ Off-Loading	85
7.2.2	Purging	85
7.2.3	Loading Operations	86
7.2.4	Cool Down of Cryogenic Systems	87
8	Transportation	89
8.1	General	89
8.1.1	Public Thoroughfare	89

8.1.2	Private Thoroughfare	89
8.1.3	DOT Definitions.	89
8.2	Transport on Public Thoroughfares	89
8.2.1	General	89
8.2.2	Training	89
8.2.3	Emergency Response	90
8.2.4	Transport Requirements for GH ₂	90
8.2.5	Transportation Requirements for LH ₂	90
8.2.6	Security Requirements for Hydrogen Transportation	90
8.3	Transport on Privately Controlled Thoroughfare	90
8.3.1	Standard Commercial Operation on Site	90
8.3.2	Noncommercial Equipment and Special Operations	91
8.3.3	Guidelines for the Design of Noncommercial Transport Equipment.	91
8.3.4	General Operating Procedures	91
8.3.5	Inspection, Certification, and Recertification of Mobile Vessels	92
8.4	Transportation Emergencies	92
8.4.1	Initial Actions	92
8.4.2	Emergency Actions	92
9	Emergency Procedures	94
9.1	General	94
9.1.1	Emergency Action Plan	94
9.1.2	Alarm System	94
9.1.3	Incident Management System	95
9.1.4	Incident Command System	95
9.1.5	Training	95
9.2	Types of Emergencies	95
9.2.1	General	95
9.2.2	Controllable Leaks	95
9.2.3	Uncontrollable Leaks	96
9.2.4	Handling Gas Leaks from Cylinders	96
9.2.5	Handling Cylinder Fires	96
9.2.6	Hydrogen Spills	96
9.3	Assistance in Emergencies	97
9.3.1	Fire and Police Departments	97
9.3.2	Site Personnel	97
9.3.3	Security	97

9.4	Fire Suppression	97
9.4.1	General	97
9.4.2	Actions against GH ₂ Fires	98
9.4.3	Actions against LH ₂ Fires	98
9.5	First-Aid for Cryogenic-Induced Injuries	99
9.5.1	Procedures	99
9.5.2	Training	99
9.6	Safeguards for Entering Permit-Required Confined Spaces	99
Annex A	Figures and Tables (Informative)	101
Annex B	3 Assessment Examples (Informative)	165
Annex C	Scaling Laws, Explosions, Blast Effects, and Fragmentation (Informative)	191
	Codes, Standards and Regulations (Informative).	
Annex E	Relief Devices (Informative)	216
Annex F	Bibliography (Informative)	222
Annex G	G Index	230
Figures		
1	Double-block-and-bleed arrangement	62
A1.1	Equilibrium percentage of para-hydrogen vs. temperature	101
A1.2	Enthalpy of normal hydrogen conversion	101
A1.3	Vapor pressure of liquefied para-hydrogen from the triple point to the NBP	102
A1.4	Vapor pressure of LH ₂ from the NBP to critical point	102
A1.5	Vapor pressure of normal and para-hydrogen below the triple point	103
A1.6	Comparison of density and bulk fluid heat capacity for slush, triple-point liquid, and NBP liquid para-hydrogen	104
A1.7	Proposed phase diagram (P-T plane) for solid hydrogen at various ortho-hydrogen mole fractions	104
A1.8	Proposed phase diagram (V-T plane) for solid normal hydrogen	105
A1.9	Specific heat (heat capacity) of saturated solid hydrogen	106
A1.10	Melting line from triple point to critical point pressure for para-hydrogen	107
A1.11	Sample MSDS for gaseous and liquefied hydrogen	118
A2.1	Flammability limits at a pressure of 101.3 kPa (14.7 psia) and a temperature of 298 K (77 °F)	126
A2.2	Effects of N_2 , He, and CO_2 diluents at 298 K (77 °F), and H_2O diluent at 422 K (300 °F) on flammability limits of hydrogen in air at 101.3 kPa (14.7 psia)	126
A2.3	Effects of halocarbon inhibitors on flammability limits of hydrogen-oxygen mixtures at a pressure of 101.3 kPa (14.7 psia) and a temperature of 298 K (77 °F)	127
A2.4	Distance for fireball radiation flux induced third degree burns per amount of fuel burned at a thermal radiation intensity of 134 kJ/m² (11.8 Btu/ft²)	127
A2 5	Radiation intensity as a function of exposure time or escape time	128

A2.6	Variation in distance from a hydrogen fire for a thermal radiation exposure of 2 cal/cm ² for an exposure duration of 10 s	
A2.7	Minimum dimensions of GH ₂ -air mixtures for detonation at 101.3 kPa (14.7 psia) and 298 K (77 °F)	129
A2.8	Detonation cell widths for hydrogen-air mixtures at 101.3 kPa (14.7 psia)	129
A2.9	Minimum initiation energy for direct detonation of hydrogen-air mixtures	130
A4.1	Flame dip as a function of stack diameter and hydrogen flow	140
A4.2	Blowout and stable flame region	140
A4.3	Flame shape in crosswinds	141
A4.4	Minimum flow rate for nonstratified, two-phase hydrogen and nitrogen flow for pipeline fluid qualities below 95% and 98%	141
A4.5	Liquid hydrogen flow rate limits to avoid excessive cooldown stresses in thick-wall piping sections such as flanges for 304 SS and 6061 Al.	
A4.6	Liquid nitrogen flow rate limits to avoid excessive cooldown stresses in thick-wall piping sections such as flanges for 304 SS and 6061 Al	143
A5.1	Charpy impact strength as a function of temperature for various materials	145
A5.2	Yield and tensile stress of 5086 Al as a function of temperature	146
A5.3	Yield and tensile stress of AISI 430 stainless steel as a function of temperature	147
A5.4	Thermal expansion coefficient of copper as a function of temperature	148
A5.5	Total linear thermal contraction as a function of temperature for several materials showing the total contraction at a given temperature as the temperature is lowered from 300 K (80 °F) to the lower temperature.	149
A6.1	Irradiance of common IR sources	
A6.2	Atmospheric IR transmission and H ₂ -air-flame emission	159
A6.3	UV/VIS/near-IR emissions	160
A6.4	Flame components	160
B1.1	Hydrogen/oxygen system schematic	165
B3.1	Flow schematic	167
B4.1	Schematic for pressure buildup example	169
B5.1	Insulated liquid hydrogen transfer line schematic	171
B5.2	Cross-sectional diagram of insulated LH ₂ transfer line	172
B5.3	Typical heat leak for various types of thermal insulation	175
B6.1	Siting schematic for the LH ₂ storage dewar	175
B7.1	Schematic for relief valve installation	177
B8.1	Hydrogen ven/flare system schematic	179
B9.1	Insulated transfer line configuration	180
B10.1	Schematic of a LH ₂ storage vessel	182
B11.1	Laboratory space schematic	184

Tables

A1.1	Selected physical, thermophysical, chemical, and combustion properties of gaseous, liquefied, slush, solid para-hydrogen	
A1.2	Fixed point properties of normal hydrogen	112
A1.3a	Thermodynamic properties of the hydrogen solid-vapor two phase region	113
A1.3b	Thermodynamic properties of the hydrogen solid-vapor two phase region	114
A1.4	Thermodynamic properties of the hydrogen solid-liquid two phase region	115
A1.5	Molar volume (cm³/mol) of compressed solid para-hydrogen	117
A1.6	Thermal expansion of solid para-hydrogen	117
A2.1	Potential ignition sources	131
A2.2	Flammability limits	132
A2.3	Effects of diluents on flammable range for hydrogen in air	132
A2.4	Inhibitor for extinction of hydrogen diffusion flames	133
A2.5	Critical radiant flux levels	133
A2.6	Hydrogen-air flammability	134
A2.7	Hydrogen-oxygen flammability	135
A3.1	Order of preference for location of GH ₂ storage systems	136
A3.2	QD requirements for nonpropellant GH ₂ systems for outdoor locations	137
A3.3	Order of preference for location of LH ₂ storage systems	138
A3.4	QD requirements for nonpropellant LH ₂ systems for outdoor locations	139
A4.1	Summary of liquefied hydrogen spill data	144
A5.1	Summary of material compatibility for hydrogen service	150
A5.2	A selection of recommended materials for typical applications	151
A5.3	Minimum temperatures and basic allowable stresses in tension for selected metals	152
A5.4	Elastic properties of selected materials at room temperature and liquid hydrogen temperature	153
A5.5	Mechanical properties of selected materials at room temperature and liquid hydrogen temperature	154
A5.6	Thermal properties of selected materials at room temperature and liquid hydrogen temperature	155
A5.7	Typical characteristics of hydrogen embrittlement types	156
A5.8	Susceptibility of materials to embrittlement in hydrogen at 10,000 psi and 72 °F	157
A5.9	Comparison of air, helium, and hydrogen exposure on selected aluminum, nickel, and copper alloys	158
A6.1	Typical hydrogen gas detectors	161
A6.2	A survey and analysis of commercially available hydrogen sensors	162
A6.3	Sensitivity limits of hydrogen detectors	162
A6.4	Typical hydrogen fire detectors	163
A7.1	Hydrogen accidents – industrial	164
A7.2	Hydrogen accidents - ammonia plants	164

A7.3	Hydrogen accidents – aerospace	164
B1.1	Detonation pressures and temperatures	166
B2.1	Deflagration pressures	166
B3.1	Liquid-lockup pressure change	168
B6.1	Minimum separation distances for siting the LH ₂ dewar in Example 6	176
D6.1	Summary of hazard locations, conditions, and QD determination methods given in DoD 605.9	212
D6.2	Selection of federal regulations for hydrogen transportation	213
E3.1	Considerations for relief devices in LN ₂ and LH ₂ pipelines	220



Foreword

Hydrogen is a lightweight, easily-ignitable element that has a wide flammability range. It is extremely valuable as a fuel for various applications ranging from rockets to automobiles. It is presently being used as a propulsion fuel in the Space Shuttle and as a reactant in the fuel cells that provide electrical power for the Space Shuttle. As with any fuel, there are hazards inherent with hydrogen's use. The users and designers of hydrogen systems must be aware of these hazards and safeguard against them. One of the goals of this technical guide is to document these hazards and the safety considerations involved in addressing them.

Although a substantial amount of information has been compiled, testing in several areas is being conducted and will continue for several years. In the interest of safety, the need for such a document is immediate. Therefore, this technical guide is released with the currently compiled information, and will be periodically updated as new data are obtained.

This AIAA Guide is based on the National Aeronautics and Space Administration (NASA) document "Safety Standard for Hydrogen and Hydrogen Systems," NASA Safety Standard (NSS) 1740.16, which established a uniform NASA process for hydrogen system design, materials selection, operation, storage, and transportation. The NASA document represented a wealth of information, knowledge, and experience gained by NASA and its contractors. This information, knowledge, and experience should be extremely valuable to industry, particularly the small or infrequent user of hydrogen who has little or no experience and staff to draw upon. The NASA document was extensively reviewed by experts at the various NASA centers, and their comments and suggestions were instrumental in making it as complete and accurate as possible. The expertise of these professionals in the area of hydrogen system hazards, materials selection, design, and operation is gratefully acknowledged.

This publication is under the purview of the Hydrogen CoS, the group responsible for determining the future of the publication and for maintaining it in a technically current state. At the time of publication, the members of the AIAA Hydrogen CoS were:

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The AIAA Standards Executive Council (Phil Cheney, Chair) accepted the document for publication in XXXX.

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Scope

Purpose

The purpose of this Guide is to provide a practical set of guidelines for safe hydrogen use. The information presented in this Guide is intended as a reference to hydrogen design and practice and not as an authorizing document. This Guide contains minimum guidelines; users are encouraged to assess their individual programs and develop additional requirements as needed.

Application

The words "shall" and "must" are used in this Guide to indicate a mandatory requirement, and the authority for the requirement is given. The words "should" and "will" are used to indicate a recommendation or that which is advised but not mandatory.

The information is arranged in an easy-to-use format. The reader will find the following useful to note:

- A numbered outline format is used so information can be readily found and easily cited.
- An index is provided to assist the reader in locating information on a particular topic.
- Acronyms are defined when introduced, and a tabulation of acronyms used in the document is provided in the Acronyms section.
- Definitions of many of the terms used in this Guide are given in the Vocabulary section.
- All sources are referenced so the user can verify original sources as deemed necessary. References
 cited in the main body of the text can be found in the bibliography in Annex F. The latest revisions of
 codes, standards, and mandatory regulations should be used when those referenced are superseded.
- The International System of Units (SI) is used for primary units, and U.S. Customary units are given in parentheses following the SI units. Some of the tables and figures contain only one set of units.



Acronyms

AHJ Authority Having Jurisdiction

AIAA American Institute of Aeronautics and Astronautics

AISI American Iron and Steel Institute
ANSI American National Standards Institute

API American Petroleum Institute

ASME American Society of Mechanical Engineers
ASTM American Society for Testing and Materials
BLEVE Boiling Liquid Expanding Vapor Explosions
BPVC Boiler and Pressure Vessel Code (ASME)

BrCF₃ Bromotrifluoromethane CCD Charge Coupled Device

CF Cubic Feet @ 101.3 kPa (14.7 psia), 294.1 K (70 °F)

CFR Code of Federal Regulations
CGA Compressed Gas Association

CH₃Br Bromomethane

CM Cubic Meters @ 101.3 kPa (14.7 psia), 294.1 K (70 °F)

CO₂ Carbon Dioxide

CoS Committee on Standards

DI Deionized water
DoD Department of Defense
DOT Department of Transportation

 $\begin{array}{lll} \text{ES} & \text{Explosion Site} \\ \text{GH}_2 & \text{Gaseous Hydrogen} \\ \text{GN}_2 & \text{Gaseous Nitrogen} \\ \text{GOX} & \text{Gaseous Oxygen} \end{array}$

H₂O Water

HCFC Hydrochlorofluorocarbons

He Helium

ICS Incident Command System

IEEE Institute of Electrical and Electronic Engineering

IMS Incident Management System

IPA Isopropyl Alcohol

IR Infrared

J-T Joule-Thomson KSC Kennedy Space

KSC Kennedy Space Center
L/D Length to Diameter
LFL Lower Flammability Limit
LH₂ Liquefied Hydrogen
LN₂ Liquefied Nitrogen
LNG Liquefied Natural Gas
LOX Liquid Oxygen

MAWP Maximum Allowable Working Pressure

MIE Minimum Ignition Energy
MSDS Material Safety Data Sheet

NASA National Aeronautics and Space Administration

N₂ Nitrogen

NBP Normal Boiling Point

NBT Normal Boiling Temperature
NFPA National Fire Protection Agency

NHB NASA Handbook NSS NASA Safety Standard NTP Normal Temperature and Pressure (absolute), 293.15 K (68 °F);

101.325 kPa (14.696 psia)

PCTFE Polychlorotrifluoroethylene Potential Explosion Site PES QD Quantity-Distance

SI International System of Units

Slush Hydrogen SLH₂ SOW Statement of Work

Std Standard

TAO Thermal Acoustic Oscillations

 TLV Threshold Limit Value

TNT Trinitrotoluene

Upper Flammability Limit UFL

Ultraviolet UV VIS Visible



Terms and Definitions

acceptance test

A standard test that leads to certification of a component or system.

attendant

An individual stationed outside one or more permit-required confined spaces who monitors the authorized entrants and who performs all attendant's duties assigned in the employer's permit-required confined space program. Authorized entrant means an employee who is authorized by the employer to enter a permit-required confined space.

authority having jurisdiction (AHJ)

Organization, office, or individual responsible for "approving" equipment, an installation, or a procedure. The designation is used in a broad manner because jurisdiction and "approval" agencies vary, as do their responsibilities. Where public safety is primary, the AHJ may be a federal, state, local, or other regional department or individual such as a fire chief, fire marshal, chief of a fire prevention bureau, labor department, health department, building official, electrical inspector, or others having statutory authority. In many circumstances, the AHJ is the property owner or his designated departmental official. At government installations, the AHJ may be the commanding officer or a designated departmental official. "Approved" is defined herein as being authorized by, or acceptable to, the AHJ.

autoignition

The phenomenon in which a mixture of gases, vapors, mists, dusts, or sprays ignites spontaneously with no external ignition source. It is frequently called autogenous ignition or spontaneous ignition.

autoignition temperature

The lowest temperature at which a material will spontaneously ignite. No additional ignition energy (ignition source) is required.

blast wave

Pressure pulse following a shock wave. It is due to velocity imparted by the shock wave to the medium particles.

BLEVE (boiling liquid expanding vapor explosion)

Liquefied gases usually (or almost always) are stored in containers at a pressure above that of the local atmosphere and, therefore, they are also at a temperature above that of their normal boiling point (NBP). This pressure gage may be less than 6.9 kPa (1 psi) for some cryogenic gas containers. The sensible heat which is, in effect, "stored" in the liquid, causes very rapid vaporization of a portion of the liquid that rapidly increases with an increase in the temperature difference between that of the liquid at the instant of container failure and the NBP of the liquid if the pressure is reduced to atmospheric, such as through container failure. This can result in vaporization of a significant quantity of the liquid in the container. Liquid vaporization is accompanied by a large liquid-to-vapor expansion. It is this expansion process that provides the energy for propagation of cracks in the container structure, propulsion of pieces of the container, and rapid mixing of the vapor and air. This results in atomization of the remaining cold liquid, and in the case of combustible liquid, in a characteristic fireball upon ignition by the fire that caused the BLEVE. Also, in the case of a combustible liquid, many of the atomized droplets burn as they fly through the air. However, it is not uncommon for the cold liquid to be propelled from the fire zone too fast for ignition to occur and fall to earth still in liquid form.

buddy system

A system of organizing employees into work groups in such a manner that each employee of the work group is designated to be observed by at least one other employee in the work group. The purpose of the buddy system is to provide rapid assistance to employees in the event of an emergency.

certification

The process that results in the documented status that qualifies a vessel or system to operate in the service for which it is intended or qualifies operating personnel for specific duties. Also refers to the document itself.

cold trap

A surface refrigerated with a cryogen, often liquefied nitrogen (LN₂), to eliminate water vapor, carbon dioxide, etc. from the gas before it reaches a vacuum pump, and to eliminate diffusion of oil particles back into the vacuum space.

cryo-pumping

A process by which gases are condensed on surfaces within an enclosure at extremely low temperatures to reduce pressures. This is usually attained by using liquid helium, liquid hydrogen, or cryogenic gaseous hydrogen, and liquid nitrogen. For the purposes of this document the context is for conditions in which components chilled by cold hydrogen inadvertently liquefy or freeze air.

cryogenic

Conditions at low temperatures, usually at or below 123 K (-239 °F).

deflagration

A flame moving through a flammable mixture in the form of a subsonic wave (with respect to the unburned mixture).

detonation

Exothermic chemical reaction coupled to a shock wave that propagates through a detonable mixture. The velocity of the shock wave is supersonic with respect to the unburned gases. After initiation, the thermal energy of the reaction sustains the shock wave, and the shock wave compresses the unreacted material to sustain the reaction.

detonation limits

The upper and lower detonation limits are the maximum and minimum concentrations of a gas, vapor, mists, sprays or dust in air or oxygen for stable detonations to occur. The limits are controlled by the size and geometry of the environment as well as the concentration of the fuel. Detonation Limit is sometimes used as a synonym for Explosive Limit.

diaphragm

A membrane that can be used as a seal to prevent fluid leakage or an actuator to transform an applied pressure to linear force.

exclusion area

An area in which personnel access, equipment, and activities are controlled. Access within an exclusion area is limited to essential personnel whose presence is necessary. Such personnel must meet specific training requirements. Equipment located within an exclusion area must meet specific requirements, such as the elimination or control of ignition sources. Activities and operations within an exclusion area must be carefully planned with the requirements of safety to personnel and reduction of risk to adjacent facilities.

explosion

The rapid equilibration of pressure between the system and the surroundings, such that a shock wave is produced. Explosions may occur through mechanical failure of vessels containing high-pressure fluids or through rapid chemical reactions producing large volumes of hot gases.

explosive yield

Energy released in an explosion. It is often expressed as a percent or fraction of the energy that would be released by the same mass of a standard high explosive such as trinitrotoluene (TNT).

failure mode and effects analysis (FMEA)

A systematic, methodical analysis performed to identify and document all identifiable failure modes at a prescribed level and to specify the resultant effect of the modes of failure.

flame velocity or flame speed

Refers to the velocity of propagation of the reaction zone through the flammable mixture, as measured by a stationary observer. Usually measured at the front of the flame.

flammability limits

The lower flammability limit (LFL) and upper flammability limit (UFL) vapor concentrations (usually reported as percent by volume) of fuel in a flammable mixture that will ignite and propagate a flame. These limits are functions of temperature, pressure, diluents, and ignition energy.

flammable

Capable of being easily ignited in air, oxygen, or other supporting atmosphere.

flammable liquid

Liquid with a flash point temperature below 300 K (80 °F) as determined by American Society of Testing and Materials (ASTM) standard methods (D56 flash point by TAG closed tester or D92 flash point by Cleveland open cup).

flash point

The lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface or within a vessel. Combustion does not continue.

fluid, liquid, gas

A pure substance, in general, may exist in any of three phases: solid, liquid, and, gas (under certain conditions all three phases may coexist). In this guide the term "fluid" may be used to refer to a gas, a liquid, or both. Two kinds of fluids are considered in this guide, compressible and incompressible. A liquid is considered incompressible, except possibly at very high pressures and/or temperatures. Gases and vapors are compressible fluids. A gas is a state of matter in which the molecules are practically unrestricted by cohesive forces. A gas has neither definite shape nor volume. A liquid is a state of matter in which the molecules are relatively free to change their positions with respect to each other but restricted by cohesive forces so as to maintain a relatively fixed volume. A cryogenic fluid is a fluid that has a normal boiling point below approximately 200 K, although this temperature is not universally accepted as the temperature for defining a cryogenic fluid.

gaseous hydrogen (GH₂) system

An assembly of components to which hydrogen is delivered, stored, and used in the gaseous form. The system may include storage vessels, piping, valves, relief devices, pumps, vacuum system, expansion joints, and gages. The nature of the working fluid (GH₂) and operating parameters, create hazards to people and the surrounding environment. A GH₂ system as defined in 29 Code of Federal Regulations (CFR) 1910.103 and National Fire Protection Agency (NFPA) 50A is limited to the bulk storage vessel (and ancillary components) from the point of the fill connection to the point where GH₂ enters the distribution piping.

hazard

Existing or potential condition that can result in, or contribute to, a mishap.

hydrostatic test

A test performed on a pressure vessel or system in which the vessel or system is filled with a liquid (usually water) and pressurized to a designated level in a manner prescribed in the applicable code.

intraline separation

The minimum distance to be maintained between operating buildings and sites within an operating line, of which at least one contains, or is designed to contain, propellants or explosives. This distance may be

reduced if equivalent protection to personnel and property is provided by building design and construction or a barricade. This distance shall be determined based on the maximum explosives weight.

intrinsically safe installation

An installation in which any spark or thermal effect, produced normally or in specified fault conditions, is incapable, under test conditions prescribed in NFPA 493, of causing ignition of a mixture of flammable material in air in its most easily ignited concentration.

liquid hydrogen (LH₂) system

An assembly of components to which hydrogen is delivered, stored, and used in the liquid and/or gaseous form. The system may include storage vessels, piping, valves, relief devices, pumps, vacuum systems, expansion joints, and gages. The nature of the working fluid (LH_2 and GH_2) and operating parameters, create hazards to people and the surrounding environment. An LH_2 system as defined in NFPA 50B is limited to the bulk storage vessel (and ancillary components) from the point of the fill connection to the point where LH_2 and/or GH_2 enters the distribution piping.

maximum allowable working pressure (MAWP)

The maximum pressure permissible at the top of a vessel in its normal operating position at the coincident operating temperature. It is the least of the values found based on calculations for every element of the vessel.

minimum spark energy for ignition

The minimum spark energy required to ignite the most easily ignitable concentration of fuel in air and oxygen.

molecular seals

A type of purge-reduction seal that relies on a set of concentric structures to prevent backflow of air via molecular weight differences in gases.

overpressure

The pressure in a blast wave above atmospheric pressure.

permit-required confined space

A confined space is not normally occupied by personnel, it has limited or restricted openings for entry and exit, may lack adequate ventilation, may contain or produce dangerous air contamination, and may not be safe for entry.

pneumatic or pneumostatic test

A test performed on a pressure vessel or system in which air or gas is introduced and pressurized to a designated level in a manner prescribed in the applicable code. Pneumatic tests are potentially hazardous and all personnel shall be excluded from the hazard zone. Pneumatic tests shall be made following an approved written test procedure.

portable tank/container

Any tank or container as defined by the U.S. Department of Transportation designed primarily to be attached temporarily to a motor vehicle, other vehicle, railroad car other than tank car, or marine vessel, and equipped with skids, mountings or accessories to facilitate handling of the container by mechanical means, in which any compressed gas is to be transported.

pressure vessel

Any vessel used for the storage or handling of gas or liquid under positive pressure. Components of systems are included, such as, heat exchanger shells and drying towers and other shell structures for which the rules of the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code (BPVC), Section VIII would apply.

proof test

A pressure test performed to establish or verify the maximum allowable working pressure of a vessel, system, or component thereof. May also be used (1) when the strength cannot be computed with a satisfactory assurance of accuracy, (2) when the thickness cannot be determined by means of the design rule of the applicable code or standard, or (3) when the critical flaw size to cause failure at the certified pressure cannot be identified by other nondestructive test methods.

quenching distance

The gap dimension required to prevent the propagation of an open flame through a flammable fuel-air mixture.

quenching gap

The quenching gap is defined as the spark gap between two flat parallel-plate electrodes at which ignition of combustible fuel-air mixtures is suppressed; smaller gaps totally suppress spark ignition. The quenching gap is the passage gap dimension requirement to prevent propagation of an open flame through a flammable fuel-air mixture that fills the passage.

recertification

The procedure by which a previously certified vessel or system, by appropriate tests, inspections, examinations, and documentation, is qualified to continue or be returned to operations at the design pressure.

rupture disk

A nonreclosing pressure-relief device designed to remain open after operation. A manual resetting means may be provided.

safety factor

The ratio, allowed for in design, between the point of failure of a member, material, structure, equipment or system, and the actual working stress or safe permissible load placed on it during ordinary use.

set pressure

The pressure marked on a safety relief valve at which the pressure relief valve is set to start to discharge.

shock

A violent collision or impact and the subsequent transmission of energy through the system. The energy moves as a wave at velocities greater than the speed of sound relative to the undisturbed material.

storage container

Any container designed to be permanently mounted on a stationary foundation and is used to store any compressed gas.

surface finish (RMS)

The degree of surface roughness as measured by the average deviation from the mean (root-mean-square value) of the maximum peak-to-valley height. The roughness values are commonly given in units of micro-inches (millionths of an inch).

tank

Any vessel used for the storage or handling of liquids for which the internal pressure is only a function of the liquid head or a combination of liquid head and vapor pressure.

Trademarks

The following commercial products that require designation are mentioned in this document. This information is given for the convenience of the users of this Guide and does not constitute an endorsement. Equivalent products may be used if they can be shown to lead to the same result.

Trademark	Company Name	Company Location
Braycote™	Bray Oil Company	Los Angeles, California
Dacron™	E.I. DuPont de Nemours, & Company	Wilmington, Delaware
Fluorogold™	Seismic Energy Products	Athens, Texas
Flurorogreen™	ATG Group	Houston, Texas
Hastelloy™	Haynes International, Inc.	Kokomo, Indiana
Heliarc™	ESAB Welding & Cutting Products	Florence, South Carolina
Inconel™	Inco Alloys International, Inc.	Huntington, West Virginia
Invar™	Carpenter Technology	Reading, Pennsylvania
Krytox™	E.I. DuPont de Nemours, E.I. & Company	Wilmington, Delaware
Monel™	Inco Alloys International, Inc.	Huntington, West Virginia
Mylar™	E.I. DuPont de Nemours, & Company	Wilmington, Delaware
Nomex™	E.I. DuPont de Nemours, & Company	Wilmington, Delaware
Teflon™	E.I. DuPont de Nemours, & Company	Wilmington, Delaware
Versilube™	General Electric Company	Schenectady, New York
Viton™	E.I. DuPont de Nemours, & Company	Wilmington, Delaware



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1 Basic Hydrogen Safety Guidelines

1.1 Introduction

This Guide contains guidelines for safely storing, handling, and using hydrogen in gaseous, liquid, or slush form, whether used as a nonpropellant or propellant. Each designer, user, operator, maintainer, quality assurance person, and designated project manager is responsible for incorporating the appropriate requirements of this guide into their projects or facilities. However, use of this guide does not relieve the designer, user, operator, maintainer, quality assurance person, or designated managers of professional responsibility or allow them to preclude the exercise of sound engineering judgment.

1.1.1 General

For the purposes of this Guide, hydrogen may refer to the gaseous (GH₂), liquefied (LH₂), or slush (SLH₂) form. Specific or special considerations for each form will be delineated.

This Guide contains sections on hydrogen properties and hazards, materials compatibility, facility design, design of components, detection, and transportation. It also covers various operational issues and emergency procedures. The material in these sections is supplemented by details and information in the following annexes in this Guide:

- Annex A provides selected (primarily safety related) chemical, physical, and combustion properties of hydrogen, and information regarding storage siting, venting and flow, materials, hydrogen and hydrogen fire detection, and accidents involving hydrogen.
- Annex B gives assessment examples to illustrate the use of selected requirements.
- Annex C describes scaling laws, explosions, blast effects, and fragmentation.
- Annex D gives information related to applicable codes, standards, and regulations.
- Annex E provides information regarding pressure relief devices and requirements.
- Annex F provides references to other source documents.
- Annex G provides an index of terms used throughout this guide.

The intent of this Guide is to provide enough information that it can be used alone, but at the same time, data sources that can provide much more detail, if required, are referenced. These sources are listed in the Bibliography.

Any information contained herein on hazards and use of hydrogen is based on current knowledge and is subject to change as more testing is completed and evaluated.

Federal and state mandatory regulations shall take precedence in the event of conflicting requirements. A general policy is that when requirements conflict, the most stringent shall apply (29 Code of Federal Regulations (CFR) 1910.120).

1.1.2 Hydrogen Usage

In this guide the use of hydrogen is separated into two categories — propellant and nonpropellant. These categories are described briefly below and more thoroughly in Section D.1.

The propellant category involves the use of hydrogen as a propellant in missile and rocket propulsion applications. The propellant category commonly involves facilities such as launching pads and static test stands, and the storage tanks associated with these facilities.

The nonpropellant category involves the use of hydrogen in a multitude of commercial, industrial, and consumer applications. These applications include the use of hydrogen: as a coolant in large turbine electrical generators; in making ammonia for fertilizer, as a feedstock in petroleum refining, petrochemical, chemical, and synthetic fuel; and in food processing, semiconductor, glass, and steel industries.

The use of hydrogen in several emerging technologies undoubtedly will result in the need for other categories in the future.

One of the major differences in the propellant and nonpropellant categories is the quantity-distance (QD) requirement for siting LH₂ facilities, especially their storage tanks. A much larger QD is required for the propellant use because of the greater hazards involved with it. Consequently, separate standards governing QD and siting requirements are specified. These standards are described in Section 1.1.3.

1.1.3 Applicable Standards

1.1.3.1 Standards for Propellant Use

The following standards and guidelines apply and shall be followed for LH₂ used as a propellant.

a) Department of Defense (DoD) 6055.9

DoD 6055.9 sets requirements for siting LH_2 storage in relation to facilities and other propellants and chemical storage and for personnel monitoring. (See Section D.5 of Annex D for more information about DoD 6055.9.

b) 29 CFR 1910.119

29 CFR 1910.119 sets requirements for hazard analysis for systems involving 4,536 kg (10,000 lb) or more of hydrogen in any form.

c) 29 CFR 1910.103

DoD 6055.9 sets requirements for siting LH_2 storage tanks that are used in propulsion applications such as missile and rocket facilities; however, it may be possible that some storage tanks at such sites could be installed in accordance with 29 CFR 1910.103 . Also, the design principles and guidelines given in 29 CFR 1910.103 could be applied to LH_2 storage tanks that are used in propellant applications.

- d) If at all possible, all pressure vessels for propellant hydrogen service shall be designed, constructed, and tested in accordance with the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code (BPVC). However, this is usually not practical for flight weight hardware, including propellant storage tanks. Flight weight hardware should be designed, constructed, and tested in accordance with appropriate standards that are applicable for aerospace pressure vessels as specified by the authority having jurisdiction (AHJ).
- e) DoD 6055.9 sets requirements for separation distances for piping containing propellants. Although DoD 6055.9 does not address piping design, construction, or testing, it is recommended by this Guide that all piping systems for propellant hydrogen service be designed, constructed, and tested in accordance with ASME B31.3 and Compressed Gas Association (CGA) G-5.4.

1.1.3.2 Standards for Nonpropellant Use

The following standards apply and shall be followed for the nonpropellant use of hydrogen.

- a) 29 CFR 1910.103
 - 29 CFR 1910.103 provides requirements for the design and operation of GH₂ and LH₂ storage systems at consumer sites. It also provides siting and QD requirements for locating storage vessels.
 29 CFR 1910.103 incorporates most of the now superceded versions of National Fire Protection Agency (NFPA) 50A and 50B.
 See Section D.4 of Annex D for more information about 29 CFR 1910.103, NFPA 50A and 50B.
 - 2) 29 CFR 1910.103 applies to:

- GH₂ hydrogen storage systems on the premises of a consumer where the supply of hydrogen to the consumer premises originates outside the consumer premises and is delivered by mobile equipment. A GH₂ storage system is defined as one into which hydrogen is delivered, stored, and discharged in the gaseous form to the consumer's piping. The system includes stationary or movable containers, pressure regulators, safety relief devices, manifolds, interconnecting piping, and controls. The system terminates at the point where hydrogen at service pressure first enters the consumer's distribution piping.
- LH₂ hydrogen storage systems on consumer premises.
- Individual GH₂ systems each having a total hydrogen content of less than 11 cubic meters (CM) (400 cubic feet (CF)) that are located less than 1.5 m (5 ft) from each other.

3) 29 CFR 1910.103 does not apply to:

- A single GH₂ system using containers having a total hydrogen content of less than 11 CM (400 CF), measured at an absolute pressure of 101.3 kPa (14.7 psia) and 294.1 K (70 °F).
- Portable containers having a total LH₂ content of less than 150 L (39.63 gal).
- A LH₂ storage capacity greater than 113,550 L (30,000 gal); this is the maximum quantity that is addressed in the QD table.
- GH₂ and LH₂ manufacturing plants or other establishments operated by a hydrogen supplier or his agent for the purpose of storing hydrogen and refilling portable containers, trailers, mobile supply trucks, or tank cars.

4) 29 CFR 1910.103 requires that:

- GH₂ containers be designed, constructed, and tested in accordance with appropriate requirements of the ASME BPVC, Section VIII, Unfired Pressure Vessels.
- LH₂ containers be designed, constructed, and tested in accordance with appropriate requirements of the ASME BPVC, Section VIII-Unfired Pressure Vessels, or applicable provisions of American Petroleum Institute (API) Standard 620 and Appendix R.
- Mobile GH₂ containers be designed, constructed, tested, and maintained in accordance with U.S. Department of Transportation (DOT) Specifications and Regulations (CFR Title 49). (Note: no explicit specifications and regulations of CFR Title 49 are specified by 29 CFR 1910.103.)
- Mobile LH₂ containers be designed, constructed, and tested, and maintained in accordance with DOT Specifications and Regulations (CFR Title 49). (Note: no explicit specifications and regulations of CFR Title 49 are specified by 29 CFR 1910.103.)
- GH₂ containers be equipped with safety relief devices as required by the ASME BPVC, Section VIII-Unfired Pressure Vessels, or the DOT Specifications and Regulations under which the container is fabricated.
- Stationary LH₂ containers be equipped with safety relief devices sized in accordance with CGA Pamphlet S-1, Part 3, Safety Relief Standards for Compressed Gas Storage Containers.
- Portable LH₂ containers complying with the DOT Regulations be equipped with safety relief devices as required by the DOT Specifications and Regulations, and that these

safety relief devices be sized in accordance with CGA Pamphlet S-1, Part 1, Compressed Gas Cylinders and Part 2, Cargo and Portable Tank Containers.

- GH₂ piping, tubing, and fittings be suitable for GH₂ service, for the pressures and temperatures involved, and conform to Section 2, "Industrial Gas and Air Piping," Code for Pressure Piping, American National Standards Institute (ANSI) B31.1, 1967 (ANSI 1967^{*}) with addenda B31.1-1969 (ANSI 1969^{*}).
- Piping, tubing, and fittings for the GH₂ parts (above -20 °F) of a LH₂ system conform to the applicable sections of Pressure Piping Section 2, "Industrial Gas and Air Piping," Code for Pressure Piping, ANSI B31.1, 1967 (ANSI 1967) with addenda B31.1-1969 (ANSI 1969). Design of LH₂ or cold (-20 °F or below) gas piping shall use Petroleum Refinery Piping ANSI B31.3-1966 (ANSI 1966a) or Refrigeration Piping ANSI B31.5-1966 (ANSI 1966b) with addenda B31.5-1968 (ANSI 1968) as a guide.
- Thermal insulating materials used in a LH₂ system shall be rated nonburning in accordance with American Society for Testing and Materials (ASTM) Procedures D1692-68.[†]
- Electrical equipment in specified locations of a GH₂ system be in accordance with Subpart S of 29 CFR 1910 for Class I, Division 2 locations.
- Electrical equipment in specified locations of a LH₂ system be in accordance with Subpart S of 29 CFR 1910 for Class I, Group B, Division 1 locations, or for Class I, Group B, Division 2 locations, as specified; or, it may be purged in accordance with NFPA No. 496, Standard for Purged and Pressurized Enclosures for Electrical Equipment.
- Portable GH₂ containers be legibly marked in accordance with "Marking Portable Compressed Gas Containers to Identify the Material Contained" ANSI Z48.1.[‡]

b) 29 CFR 1910.119

29 CFR 1910.119 sets requirements for hazard analysis for systems involving 4,536 kg (10,000 lb) or more of hydrogen in any form.

c) All piping systems for nonpropellant hydrogen service should be designed, constructed, and tested in accordance with ASME B31.3 and CGA G-5.4.

1.1.3.3 Standards for Slush and Solid Hydrogen

No standards specifically apply to SLH_2 and solid hydrogen at present. It is suggested that when the total mass of these materials in the system being considered is equivalent to the amounts cited in 1.1.3.1 and 1.1.3.2 that these reference standards be applied as appropriate considering the increased hazards involved with SLH_2 and solid hydrogen. Except for supplying limited property data in Section 2 and Annex A, solid hydrogen is not discussed further in this Guide.

An early version of this standard is referenced here and in Annex F, and should be consulted for further information related to this section.

[†] ASTM D1692-68, *Test for Flammability of Plastic Sheeting and Cellular Plastics,* from the American Society for Testing Materials (ASTM) (1968) has been withdrawn and is no longer available.

[‡] ANSI Z48.1, *Marking Portable Compressed Gas Containers to Identify the Material Contained,* from ANSI. (1954) has been superseded by CGA C-7, *Guide to Preparation of Precautionary Labeling and Marking of Compressed Gas Containers*.

1.1.3.4 Standards for Minimum Quantities

The AHJ shall establish requirements for safe storage and use that shall protect all personnel and facilities, for hydrogen systems in quantities below the minimum quantity specified in the standards and guidelines cited above.

1.1.3.5 Standards for Other Facilities, Equipment, and Test Articles

Those facilities, equipment, and test articles that do not meet the definitions of GH₂ or LH₂ systems as stated in the standards and guidelines cited above but are in hydrogen service should have applied for their design, construction, testing, and use 29 CFR 1910.103, 29 CFR 1910.119, DoD 6055.9, and other standards as directed by the AHJ. Additional recommendations for safe gaseous and liquid hydrogen vent system operations are presented in the Compressed Gas Association publication *Hydrogen Vent Systems* (CGA G-5.5).

1.1.3.6 Retroactive Application of Standards

- a) An existing system for nonpropellant hydrogen use that is not in strict compliance with the provisions of the standards and guidelines cited above may be permitted to be continued in use where such use does not constitute a distinct hazard to life or adjoining facilities (NFPA 50A and 50B).
- b) Existing facilities, and those approved for construction under editions of DoD 6055.9 previous to the latest edition, wherein LH₂ is used as a propellant, that are not in compliance with the current edition of DoD 6055.9, may continue to be used for the balance of their functional lives, as long as current operations present no significantly greater risk than that assumed when the facility was originally designed, and it can be demonstrated clearly that a modification to bring the facility into compliance is not feasible (DoD 6055.9). It is recommended by this Guide that such a facility should be brought into compliance with the current standards in the case of a major renovation.

1.2 Applicable Documents

Information on safe use of hydrogen systems is cited in each section of this Guide. Unless otherwise specified, the latest revision of documentation shall be used. The latest revision applies in the event of conflict. Unit conversions are consistent, to the extent possible, with Institute of Electrical and Electronic Engineers (IEEE)/ASTM Standard (Std) S-10.

1.3 Personnel Training

1.3.1 Hydrogen Handling Training

Personnel handling hydrogen or designing equipment for hydrogen systems must become familiar with the physical, chemical, and specific hazardous properties of GH₂, LH₂, and SLH₂. Training should include detailed safety programs that recognize human capabilities and limitations. A primary goal of a safety program is to eliminate accidents and to minimize the severity of accidents that occur. Annex B, Example 12 provides a summary of typical information that may be presented in training/certification of liquid hydrogen handlers. Operators must be kept informed of any changes in safety procedures and facility operations.

29 CFR 1910. 1200 applies to any chemical (including hydrogen) that presents a physical or health hazard to personnel, and requires that personnel receive training regarding any such chemical and its hazards involved in their work area. This training is part of the Hazard Communication Program that is described in Section 1.3.4. For example, a written record of personnel training is required in parts of the Code of Federal Regulations (CFR), such as 29 CFR 1910.119.

1.3.2 Designer Training

Personnel involved in equipment design and operations planning must be trained to carefully adhere to accepted standards and guidelines and comply with the regulatory codes as specified by the AHJ.

1.3.3 Operator Certification

Operators must be certified for handling GH₂, LH₂, and SLH₂, as appropriate, and in the emergency procedures for spills and leaks. Appropriate records of personnel training and certification must be kept.

29 CFR 1910.103 requires that "a qualified person shall be in attendance at all times while the mobile hydrogen supply unit is being unloaded." The certification of operators to perform operations involving hydrogen, such as that mentioned in the above quote from 29 CFR 1910.103, provided a procedure to determine, and to document, that they are "qualified" to do such a task. 29 CFR 1910.119 requires that the training program assure that a person can perform the assigned tasks in a safe manner. Although it does not apply to hydrogen, 29 CFR 1910.120 specifies that personnel that have received and successfully completed training and field experience shall be certified by their instructor and a written certificate shall be given to each certified person.

1.3.4 Hazard Communication Program

The AHJ, at an installation where hydrogen is handled, shall develop, implement, and maintain at the workplace, a written hazard communications program for all hydrogen operations (29 CFR 1910.1200).

1.3.5 Annual Review

All hydrogen operations being performed at an installation should be reviewed periodically (at least annually) to ensure that the safety training program is working effectively and to identify and enter into the program all potentially hazardous jobs in addition to jobs designated mandatory. Employee safety committees, employee representatives, and other interested groups should be provided an opportunity to assist in the identification process.

1.4 Inherent Safety Features

1.4.1 Hazard Management

Hazard management must be exercised for all hydrogen systems and operations regardless of the quantity of hydrogen involved. Hazard management should include techniques such as providing adequate ventilation, designing and operating to prevent leakage, and eliminating potential ignition sources.

1.4.2 Barriers

Barriers or safeguards should be provided to minimize risks and control failures.

1.4.3 Safety Systems

Safety systems should be installed to detect and counteract or control the possible effects of events such as vessel failure, leaks and spills, embrittlement, collision during transportation, vaporization system failure, ignition, fire and explosion, cloud dispersion into an unwanted location, and the exposure of personnel to cryogenic or flame temperatures.

1.4.4 Safe Interface

A safe interface must be maintained under normal and emergency conditions so at least two failures occur before hazardous events could lead to personnel injury, loss of life, or major equipment or property damage.

1.5 Controls

1.5.1 Warning Systems

Warning systems should be installed to detect abnormal conditions, measure malfunctions, and indicate incipient failures. Warning system data transmissions with visible and audible signals should have sufficient redundancy to prevent any single-point failure from disabling the system.

1.5.2 Flow Controls

Safety valving and flow regulation should be installed to adequately respond for protection of personnel and equipment during hydrogen storage, handling, and use.

1.5.3 Safety Features

System and equipment safety features should be installed to automatically control the equipment required to reduce the hazards suggested by the triggering of the caution and warning systems. Manual controls within the systems should be constrained by automatic limiting devices to prevent over-ranging.

1.6 Fail-safe Design

1.6.1 Certification

The equipment, power, and other system services shall be verified for safe performance in the design and normal operational regimes through certification.

1.6.2 Fail-Safe Design

Any failure from which potentially hazardous conditions are a risk shall cause the system to revert to conditions that will be safest for personnel and with the lowest property damage potential.

1.6.3 Redundant Features

This Guide recommends that redundant safety features (such as relief valves, instrumentation, and controls) be installed when the failure of a single safety feature could cause a mishap, which might result in loss of mission, property, or personnel.

1.7 Safety Assessment and Mishap Reporting

1.7.1 Safety Review

All plans, designs, and operations associated with hydrogen use must be subject to an independent safety review. Safety reviews should be conducted on effects of fluid properties, training, escape and rescue, fire detection, and fire fighting. A safety review is required by 29 CFR 1910.119.

1.7.2 Operating Procedures

Operating procedures for normal and emergency conditions shall be established and reviewed as appropriate. Written operating procedures are required by 29 CFR 1910.103 and 29 CFR 1910.119.

1.7.3 Hazard Analyses

Hazard analyses shall be performed to identify conditions that may cause injury, death, mission delay or loss, or property damage. A hazard analysis is required by 29 CFR 1910.119 and 29 CFR 1910.1200.

1.7.4 Mishap Reporting

Reporting, investigating, and documenting the occurrences, causes, and corrective action required for mishaps, incidents, test failures, and mission failures shall follow established basic policy procedures and guidelines as specified by the AHJ. Mishap investigation and reporting is required by 29 CFR 1910.119.

1.8 Waiver Provisions

Although this is a guide, it contains required safety provisions noted by "shall" and "must." The actions indicated are required by standards and regulations and are to be followed to prevent loss of life, injury, or property damage. Waivers to required safety provisions shall be handled and reviewed in accordance with local procedures as specified by the AHJ.

Actions specified by "should" are recommended guidelines and also denote additional safety considerations.



2 Properties and Hazards of Hydrogen

2.1 General Properties

Hydrogen is a colorless, odorless, tasteless, flammable, nontoxic gas. It is the lightest of all gases. Hydrogen can produce suffocation by diluting the concentration of oxygen below levels necessary to support life.

Liquid hydrogen is colorless, odorless, noncorrosive and not significantly reactive. LH_2 has the lowest density of any liquefied gas. It expands approximately 850 times upon conversion to a gas at normal temperature and pressure (NTP).

Hydrogen is used as a reducing agent in chemical processes.

Hydrogen is noncorrosive and considered nonreactive, but it will generally reduce the mechanical properties of some metals by a complex process commonly referred to as hydrogen embrittlement.

2.2 Ortho- and Para-Hydrogen

Hydrogen is commonly an equilibrium mixture of ortho-hydrogen and para-hydrogen. The hydrogen molecule exists in two forms, distinguished by the relative rotation of the nuclear spin of the individual atoms in the molecule. Molecules with spins in the same direction (parallel) are called ortho-hydrogen; and those with spins in the opposite direction (antiparallel) are called para-hydrogen. Figure A1.1 shows that the ortho-hydrogen will convert to para-hydrogen as the temperature of hydrogen is lowered. The equilibrium mixture of ortho- and para-hydrogen at any temperature is referred to as equilibrium hydrogen. The equilibrium ortho-para-hydrogen mixture with a content of 75% ortho-hydrogen and 25% para-hydrogen at room temperature is called normal hydrogen. The ortho-para-hydrogen conversion is accompanied by a release of heat, 703 J/g (302.4 Btu/lb) at 20 K (-423 °F) for ortho- to para-hydrogen conversion, or 527 J/g (226.7 Btu/lb) for normal to para-hydrogen conversion (Figure A1.2). Unless catalyzed, this conversion is slow but occurs at a finite rate (taking several days to complete) and continues even in the solid state. Catalysts are used to accelerate this conversion in LH₂ production facilities, which produce almost pure (95%) para-hydrogen liquid.

There are some property differences in the different forms of hydrogen; thus, one must observe for which form the data are given. The ortho- and para-hydrogen molecules have slightly different physical properties, but are chemically equivalent; therefore, the hazards associated with the use of hydrogen are the same irrespective of the molecular form.

2.3 Thermophysical Properties

Selected thermophysical properties of various states of hydrogen, primarily para-hydrogen, are given in the figures and tables in Annex A1. McCarty, Hord, and Roder (1981) provide an extensive tabulation of the thermophysical properties of hydrogen.

The vapor pressure of liquefied para-hydrogen as a function of temperature from the triple point to the normal boiling point (NBP) is shown in Fig. A1.3, and from the NBP to the critical point in Fig. A1.4. Figure A1.5 gives the vapor pressure of para-hydrogen and normal hydrogen below the triple point. Figure A1.6 gives a comparison of the densities and bulk fluid heat capacities for slush, triple-point liquid, and NBP liquid para-hydrogen. Figure A1.7 shows a proposed phase diagram (P-T plane) for solid hydrogen at various ortho mole fractions. Figure A1.8 gives a proposed phase diagram (V-T plane) for solid normal hydrogen. Figure A1.9 shows the specific heat (heat capacity) of saturated solid hydrogen. Figure A1.10 gives the melting line from the triple point to the critical point pressure for para-hydrogen. Selected thermophysical, chemical, and combustion properties of para-hydrogen are provided in Table A1.1. This table presents property data for gaseous, liquid, slush, and solid phases. Table A1.2 gives some fixed point properties of normal hydrogen. Table A1.3 gives a tabulation of thermodynamic properties of the hydrogen solid-vapor two-phase region, and Table A1.4 gives a tabulation of the

thermodynamic properties of the hydrogen solid-liquid two-phase region. Table A1.5 gives some data on the molar volume of compressed solid para-hydrogen. Table A1.6 gives the thermal expansion coefficient of solid para-hydrogen from 1 to 13.8 K (-458 to -435 °F).

The thermodynamic properties of liquid and vapor hydrogen in the normal and para state can be calculated with computer programs from the National Institute of Standards and Technology (NIST) and commercial companies.§

2.4 Health Hazard Properties

Hydrogen is nontoxic and has no threshold limit value (TLV). Hydrogen is not listed as a carcinogen by the National Toxicology Program, International Agency Research on Cancer, or Occupational Safety and Health Administration. Health hazard data are given in the Material Safety Data Sheet (MSDS) for GH₂ and LH₂ in the Addendum to Annex A1.

Hydrogen is classified as a simple asphyxiant and can result in asphyxiation by diluting the oxygen required in breathing air. An atmosphere containing oxygen at a concentration of less than 19.5% by volume is considered oxygen deficient.

Hydrogen gas is colorless, odorless, and not detectable in any concentration by human senses; consequently, it is necessary to rely upon an instrument of some type to detect its presence.

Hydrogen burns with an almost invisible bluish flame. In daylight the flame is so pale that the first indication of a hydrogen flame may be the feeling of heat or being burned rather than seeing the flame. The thermal radiation from a hydrogen flame is such that the flame may not be felt until direct contact with the flame is made.

Cryogenic burns are possible from contact with LH_2 , cold GH_2 , or cold surfaces associated with either LH_2 or cold GH_2 . Eyes can be injured by exposure to the cold gas or splashed liquid too brief to affect the skin of the hands or face. Contact between bare parts of the body with uninsulated piping or storage vessels containing LH_2 or cold GH_2 can cause the flesh to stick and to tear when an attempt is made to break the contact.

2.5 Characteristic Properties of GH₂

While knowledge of the general chemical and physical properties of hydrogen must be available to the designer and operators of hydrogen systems, some characteristic properties of GH_2 are of particular concern for hazard analyses. The characteristics and properties of particular concern are discussed in the subsections of Section 2.5.

2.5.1 Buoyancy

The specific gravity at NTP of hydrogen and air is 0.0695 and 1.0, respectively. Therefore, hydrogen gas, at temperatures above 23 K (-418.6 °F), is lighter than NTP air and tends to rise. Saturated hydrogen vapor is heavier than air and will remain close to the ground until the temperature rises. Buoyant velocities are related to the difference in air and hydrogen densities; therefore, the cold, dense hydrogen gases produced by LH_2 spills will not rise. The buoyant velocity of hydrogen in NTP air is 1.2 to 9 m/s (3.94 to 29.5 ft/s) (McCarty, Hord, and Roder 1981).

2.5.2 Diffusion Coefficient in Air

The diffusion coefficient for hydrogen in air (both at NTP) is 0.61 cm²/s (0.095 in²/s) (McCarty, Hord, and Roder 1981).

§ The Standard Reference Data program is available from the NIST at http://www.nist.gov/srd/nist12.htm.

2.5.3 Joule-Thomson Expansion

Most gases at ambient temperature are cooled by throttled expansion from high to low pressure. However, the temperature of hydrogen increases when it is expanded at a temperature and pressure outside the temperature and pressure conditions that define the Joule-Thompson (J-T) inversion curve for hydrogen. The maximum inversion temperature for hydrogen is 202 K (-96 °F) at an absolute pressure of zero (Walker 1983); consequently, at any temperature and pressure condition greater than this, the temperature of hydrogen will increase upon expansion. The temperature increase as a result of a J-T expansion is not normally sufficient to be the source of ignition for a combustible hydrogen/oxidizer mixture. An example of the extent of the temperature rise is that the temperature of hydrogen initially at 300 K (80 °F) increases to 346 K (163 °F) when expanded from an absolute pressure of 100 MPa (14,500 psi) to an absolute pressure of 0.1 MPa (14.5 psi). A temperature rise of 46 K (83 °F) does not raise hydrogen to its ignition temperature unless it is already near the autoignition temperature of 858 K (1,085 °F).

2.6 Characteristic Properties of LH₂

All of the hazards that exist with GH_2 also exist with LH_2 because of the ease with which the liquid evaporates. Characteristic properties of LH_2 also of particular concern for hazard analyses are discussed in the following subsections of Section 2.6.

2.6.1 Boiling Point

 LH_2 has an NBP of 20.3 K (-423.5 °F) at sea level. Any LH_2 splashed on the skin or in the eyes can cause serious burns by frostbite or hypothermia. Inhaling vapor or cold gas produces respiratory discomfort and asphyxiation can result.

2.6.2 Ice Formation

Vents and valving from storage vessels and dewars may be blocked by accumulations of ice formed from moisture in the air. Excessive pressure may then rupture the container and release hydrogen.

2.6.3 Liquid Air Formation

Air in contact with uninsulated surfaces cooled by LH_2 or cold hydrogen gas below about 82 K (-312 °F) can condense. This condensate will be enriched to about 50% oxygen. Any subsequent evaporation of the condensate can result in even further oxygen enrichment. Materials in the presence of an oxygenenriched atmosphere can (depending on the material and various conditions) become combustible and some can react explosively.

2.6.4 Solidification of Contaminants

Storage vessels and other containers should be kept under positive pressure to prevent air from entering. LH_2 is subject to contamination with air condensed and solidified from a variety of sources, such as improper purging. The amount of oxygen can buildup during repeated refilling or pressurization of permanent LH_2 storage vessels. This mixture is easily ignited and can then detonate. Nitrogen, often used as a purge gas, can also be condensed and solidified, and the solid particles of nitrogen can cause damage to components or cause failures such as preventing a valve from closing completely.

2.6.5 Continuous Evaporation

The continuous evaporation of LH_2 in a vessel generates GH_2 , which must be vented to a safe location or temporarily confined safely. The gas generated by the evaporation of LH_2 will eventually warm to the ambient temperature giving a significant pressure rise if it is confined, as in a pipe between two valves. Considering GH_2 as an ideal gas, the pressure resulting from a trapped volume of LH_2 vaporizing and being heated to 294 K (70 °F) is 85.8 MPa (12,452 psia). However, the pressure is 172 MPa (25,000 psia) when hydrogen's compressibility is considered. A significant pressure increase will occur in

a system with only one phase present and the LH₂ experiences a temperature increase. A sample calculation for such a system is given in Example 3 of Annex B.

2.6.6 Buoyancy

The higher density of saturated vapor may cause a hydrogen cloud to flow horizontally or downward immediately upon release if an LH₂ spill or leak occurs, or gas at a temperature below 193 K (-112 °F) is vented (see Section 2.5.3).

2.6.7 Electric Charge Accumulation

Willis (1966) measured the electrical conductivity of LH_2 and found typical resistivities to be about 1019 ohm-cm at 25 V and that the resistivity was a linear function of applied voltage. As Willis (1966) points out, this indicates that it is not strictly correct to consider the electrical conductivity of LH_2 in terms of Ohm's Law. Although a current can be passed through LH_2 , this current can be explained in terms of charge carriers formed by background radiation. Thus, the current carrying capacity is small and more or less independent of the imposed voltage. Investigation has shown that electric charge build up in flowing LH_2 is not a great concern.

2.7 Characteristic Properties of SLH₂

 SLH_2 is a mixture of solid and LH_2 at the triple point temperature. Properties of a 50% by mass solid or 50% by volume solid mixture usually are given, although other mass (or volume) fraction mixtures of solid and liquid are possible.

All the hazards that exist with GH_2 and LH_2 also exist with SLH_2 . Additional system components are required to handle the two-phase SLH_2 ; therefore, transfer and storage operations become more complex. Characteristic properties of SLH_2 also of particular concern for hazard analyses are discussed in the following subsections of Section 2.7.

2.7.1 Vapor Pressure

The vapor pressure of SLH₂ is 7.04 kPa (1 psia). Therefore, a SLH₂ system is designed structurally to operate at pressures below atmospheric and greater care must be taken during operations to prevent air leakage into the system.

2.7.2 Volume Change

Heat leakage into SLH₂ without ullage present requires the continual addition of high solids fraction SLH₂ and the removal of LH₂ because SLH₂ expands as it degrades. Significant increases in volume can occur when the solid phase of SLH₂ melts (see Annex B, Example 3).

2.7.3 Thermal Stratification

Thermal stratification of SLH_2 storage can occur by design (a layer of LH_2 on top of the SLH_2 rising in temperature to 20.27 K (-423.5 °F) and an equilibrium pressure of 101.3 kPa (14.7 psia)), or by operation (such as the introduction of helium (He) into the ullage space for pressure control). Upsetting of the thermal stratification can lead to hazardous pressure changes in both cases.

2.7.4 Thermal Acoustic Oscillation

Thermal acoustic oscillations (TAO) can occur whenever a long tube connects a region at cryogenic temperature with an ambient-temperature region (300 K). Instrumentation lines and ports for fluid flow are examples where these conditions can exist. TAO is of concern for liquid hydrogen because of the low temperature and other pertinent thermophysical properties. TAO can occur without any net flow of fluid or any intended transfer of heat. (Edeskuty and Stewart 1996) TAO can lead to pressure surges in LH₂ and SLH₂ systems. Egress of LH₂ or SLH₂ into warmer instrument or discharge lines causes vaporization and

a pressure increase, which forces the LH₂ or SLH₂ gas back to the bulk LH₂ or SLH₂ where cooling causes a reverse surge. An oscillation such as this results in an increased heat input to the bulk LH₂ or SLH₂.

2.7.5 Aging

Aging of the solid hydrogen particles in SLH₂ could result in particle settling or change in critical flow velocity of the SLH₂. Subsequent settling would result in overpressurization of the SLH₂ flow.

2.7.6 Electric Charge Buildup

While investigation has shown that electric charge buildup in flowing LH₂ is not a great concern, the accumulation of electric charge in flowing SLH₂ has not been definitively excluded. The elimination of ignition sources might be compromised during SLH₂ flow operations.

2.7.7 Ortho- to Para-Hydrogen Conversion

The product is at least 95% para-hydrogen in normal production of LH₂. The equilibrium content of para-hydrogen at SLH₂ temperature 13.8 K (-435.2 °F) is 100%; therefore, any ortho-hydrogen will be converted to para-hydrogen. The heat generation by this residual ortho-to-para conversion acts as an additional heat leak into the system. This conversion is slow, but finite if no catalyst is present. At 20 K (-424 °F) the heat of conversion for normal hydrogen is 527 J/g (226 Btu/lb). Annex B, Example 4 contains an analysis of heat leak and ortho-para conversion in a SLH₂ system.

2.7.8 Helium Solubility

The solubility of helium in SLH₂ is a concern if helium is used to pressurize the SLH₂ storage vessel. Potential safety issues include altering the helium pressurization gas requirements (and hence pressure control), influencing the temperature gradient within the vapor phase of storage vessel (effecting helium pressurization gas requirements), and changing the pumping characteristics of the SLH₂. Although it has not been determined for SLH₂, several reports are available for the solubility of helium in LH₂ over a range of temperature and pressure (Smith 1952; Streett, Sonntag, and Van Wylen 1964).

2.8 Combustion-Related Properties

2.8.1 General

It is necessary for hydrogen to be mixed with an oxidant, that the mixture be within flammability limits, and that an appropriate ignition source be present for hydrogen to burn. Leaks and accumulations can occur even with the best efforts to contain hydrogen. The safe procedure is to eliminate all likely sources of ignition or place them away from areas of possible hydrogen leakage.

Some selected combustion-related properties of hydrogen are given in the figures and tables of Annex A.2. A brief discussion of some important combustion related properties of hydrogen is presented in the following subsections of Section 2.8.

2.8.2 Lack of Flame Color

A hydrogen-air-oxygen flame is colorless, and any visibility is caused by impurities. At reduced pressures a pale blue or purple flame may be present. Severe burns have been inflicted on persons exposed to hydrogen flames resulting from the ignition of hydrogen gas escaping from leaks.

2.8.3 Flame Temperature in Air

The flame temperature for 19.6% by volume hydrogen in air is 2,321 K (3,718 °F). Table B.2 in Annex B gives the calculated characteristics of several mixtures of hydrogen-air-oxygen using the Gordon-McBride code (Gordon and McBride 1994).

2.8.4 Burning Velocity in NTP Air

The burning velocity in NTP air, defined as the subsonic velocity at which a flame propagates through a flammable fuel-air mixture, is 2.70 to 3.50 m/s (8.86 to 11.48 ft/s). The burning velocities are affected by pressure, temperature, and mixture composition. The high burning velocity of hydrogen indicates its high explosive potential and the difficulty of confining or arresting hydrogen flames and explosions.

2.8.5 Thermal Energy Radiated from Flame to Surroundings

Exposure to hydrogen fires can result in significant damage from thermal radiation. Thermal radiation is affected by the amount of water vapor in the atmosphere.

Atmospheric moisture absorbs thermal energy radiated from a fire and can reduce the values. This effect is significant for hydrogen fires. The intensity of radiation from a hydrogen flame at a specific distance depends heavily on the amount of water vapor present in the atmosphere and is expressed as:

$$I = I_0 e^{-0.0046wr}$$
 (1)

where:

 I_0 = initial intensity (energy/time (area))

w = water vapor (% by weight)

r = distance (meters)

Figure A2.6 shows additional data on the effect of water vapor on radiant energy from hydrogen fires. The effects of thermal radiation exposure on several materials are given in Table A2.5.

2.8.6 Limiting Oxygen Index

The limiting oxygen index is the minimum concentration of oxygen that will support flame propagation in a mixture of fuel, air, and nitrogen. For example, no mixture of hydrogen, air, and nitrogen at NTP conditions will propagate flame if the mixture contains less than 5% by volume oxygen.

2.8.7 Ignition

2.8.7.1 General

Hydrogen can be easily ignited. An almost imperceptible spark or a static electricity discharge may ignite a combustible mixture of hydrogen and an oxidizer (such as air). Two important properties related to ignition are: 1) autoignition temperature and 2) minimum spark energy for ignition.

2.8.7.2 Autoignition Temperature

Hydrogen is only slightly more difficult to ignite in air than in oxygen. Ignition temperatures are dependent on GH_2 concentration and pressure and the surface treatment of containers. The reported temperature is very dependent on the system and values selected should be applied only to similar systems. At 101.3 kPa (14.7 psia) the range of reported autoignition temperatures for stoichiometric hydrogen in air is 773 to 850 K (932 to 1,070 °F); in stoichiometric oxygen it is 773 K to 833 K (932 °F to 1,039 °F). At pressures from 20 to 50 kPa (2.9 to 7.25 psia) GH_2 air ignitions have occurred at 620 K (657 °F).

2.8.7.3 Minimum Spark Energy for Ignition

Minimum spark energy for ignition is defined as the minimum spark energy required to ignite the most easily ignitable concentration of fuel in air and oxygen. The minimum spark energy for ignition of hydrogen in air is:

- 0.017 mJ (1.6 x 10⁻⁸ Btu) at 101.3 kPa (14.7 psia)
- 0.09 mJ (8.5 x 10⁻⁸ Btu) at 5.1 kPa (0.735 psia)

0.56 mJ (5.31 x 10⁻⁷ Btu) at 2.03 kPa (0.294 psia).

The minimum spark energy required for ignition of hydrogen in air is considerably less than that for methane (0.29 mJ) or gasoline (0.24 mJ). However, the ignition energy for all three fuels is sufficiently low that ignition is relatively certain in the presence of any weak ignition source, such as sparks, matches, hot surfaces, or open flames. Even a weak spark caused by the discharge of static electricity from a human body may be sufficient to ignite any of these fuels in air.

2.8.8 Quenching Gap in NTP Air

The quenching gap for hydrogen in NTP air is 0.6 mm (0.024 in.). This value is determined as the greatest physical channel dimension for which flames still cannot propagate throughout the channel (Strehlow 1983). This dimension depends on the temperature, pressure, and composition of the combustible gas mixture and the electrode configuration.

Faster burning gases generally have smaller quenching gaps; flame arresters for faster burning gases require smaller apertures. The lowest reported quenching distance for hydrogen is 0.076 mm (0.003 in.) (Wionsky 1972).

There are three major considerations in determining the quenching distance for a gaseous fuel such as hydrogen: ignition energy, mixture ratio, and pressure.

- 1) Quenching gap is a function of ignition energy. Low ignition energy, 0.001 mJ (9.5 x 10⁻¹⁰ Btu), corresponds to a small gap, 0.01 cm (0.0039 in.). Likewise, high ignition energy, 10 mJ (9.5 x 10⁻⁶ Btu), requires a larger gap, 1 cm (0.39 in.) (Van Dolah et al. 1963).
- 2) Pressure and composition affect the quenching distance. The quenching distance increases dramatically at very low pressures. At a distance of several inches, the pressure is barely sufficient to support combustion. The effect of mixture ratios is less well known; however, it appears to be constant for a given pressure between the upper flammability limit (UFL) and lower flammability limit (LFL) (Van Dolah et al. 1963).
- 3) Specific values for hydrogen-air mixtures are not available; however, the effect of pressure as a function of tube diameter for deflagration and detonation of acetylene-air mixtures can be used as a guideline (Zebetakis and Burgess 1961).

2.8.9 Flammability

2.8.9.1 Flammable Mixtures

Mixtures of hydrogen with air, oxygen, or other oxidizers are highly flammable over a wide range of compositions. The flammability limits, in percent by volume of hydrogen, define the range over which fuel vapors will ignite when exposed to an ignition source of sufficient energy. Flammability limits are dependent on the ignition energy, temperature, pressure, presence of diluents, and size and configuration of the equipment, facility, or apparatus.

A flammable mixture may be diluted with either of its constituents until the mixture concentration falls outside the flammability limits, either below the (LFL) or above the (UFL). The flammability range for hydrogen-air and hydrogen-oxygen mixtures is broadest for upward flame propagation and narrows for downward flame propagation.

LH₂ or SLH₂ as fuel, and liquid oxygen (LOX) or solid oxygen as oxidizer, do not react on contact. Mixtures of these materials have ignited during the mixing process because the energy required to ignite them is so small (Bunker, Dees, and Eck 1995). LH₂ and LOX have been detonated by an externally generated shock wave. Comparable experimental examination of SLH₂ systems does not exist.

2.8.9.2 Flammability Limits

2.8.9.2.1 General

Flammability limits of hydrogen in dry air and in oxygen at 101.3 kPa (14.7 psia) and ambient temperature are listed below in Table 1:

Table 1 — Flammability Limits of Hydrogen

Mixture	LFL*	UFL*
Hydrogen in dry air	4.1%	74.8 %
Hydrogen in oxygen	4.1 %	94 %
*At 101.3 kPa (14.7 psia) and ambient temperature		

These limits apply for upward propagation in tubes. Table A2.2 lists the effect of propagation direction. A reduction in pressure below 101.3 kPa (14.7 psia) tends to narrow the range of flammability by raising the lower limit and lowering the upper limit (Table A2.2).

2.8.9.2.2 Hydrogen-Air Flammability Limits

Hydrogen-air flammability data are presented in Table A2.6 to illustrate the range of behavior typical of hydrogen mixtures under different conditions.

Table A2.6 presents data generally in order of increasing pressure. Several data are presented for ambient pressure to show the effects of propagation direction and temperature. Flammability behavior for a given variable is often correlated against mixture composition. This data typically appears as a U-shaped curve where the base of the "U" represents near stoichiometric mixtures and the tails of the "U" represent lean or rich compositions. For near stoichiometric mixtures the low-pressure limit approaches 7-kPa and the upper and lower flammability limits are 64% and 4% by volume respectively (reference c in Table A2.6) for small energy ignition sources (45 mJ). The low-pressure limit can be decreased by a factor of 50 and the flammability limits expanded (reference d in Table A2.6) by using very high-energy ignition sources. Under ambient conditions stoichiometric mixtures are extremely sensitive and can be ignited very small energies. Ignition in mixtures, under lean conditions of less than 10% hydrogen by volume, results in low temperatures and incomplete combustion of the reactants. The flammability range increases when the initial temperature of the mixture is increased. The flammability range decreases for downward flame propagation. As the initial pressure of reactants is increased, the flammability limits decrease by several percent for pressures in the range of 1 to 2 MPa and expand for higher pressures.

2.8.9.2.3 Hydrogen-Oxygen Flammability Limits

Hydrogen-oxygen flammability data are presented in Table A2.7 to illustrate the range of behavior typical of hydrogen mixtures under different conditions.

Table A2.7 presents data generally in order of increasing pressure. Several data are presented for ambient pressure to show the effects of propagation direction and temperature. The behavior trends for hydrogen-oxygen mixtures generally parallel those for hydrogen-air; however, the greater reactivity of hydrogen-oxygen mixtures results in a lower minimum ignition energy (MIE) and expanded flammability limits. The only exception to the parallel behavior is that no reduction followed by expansion of the flammability limits occurs at greater than ambient pressures.

2.8.9.2.4 Effects of Diluents

Figure A2.1 shows the flammability limits for hydrogen-oxygen-nitrogen. Table A2.2 shows flammability limits for GH_2 and gaseous oxygen (GOX) with equal concentrations of added inert gases (helium (He), carbon dioxide (CO_2), and nitrogen (N_2)). Table A2.3 shows the qualitative effect of He, CO_2 , N_2 , and Argon (Ar) diluents for various tube sizes. Argon was the least effective in reducing the flammable range for hydrogen in air.

Figure A2.2 shows the effects of He, CO_2 , N_2 , and water vapor on the flammability limits of hydrogen in air. Measurements were performed at 298 K (77 °F) and 101.3 kPa (14.7 psia) except for the water vapor studies, which were performed at 422 K (300 °F). Water was the most effective in reducing the flammability range, and helium was the least effective.

2.8.9.2.5 Effects of Halocarbon Inhibitors

Figure A2.3 shows the effects of halocarbon inhibitors on the flammability limits of hydrogen-oxygen mixtures.

Table A2.4 compares the effect of N₂, Bromomethane (CH₃Br), and Bromotrifluoromethane (BrCF₃) required to extinguish hydrogen diffusion flames in air. The inhibitors were more effective when added to the air stream; nitrogen was more effective when added to the fuel stream.

2.9 Flame Propagation

2.9.1 General

Rapid flame propagation and explosion are possible when a flammable hydrogen-oxidizer mixture fills a region or volume. Combustion of a hydrogen-oxidizer mixture can occur by two different processes: deflagration and detonation. Deflagration can occur in mixtures within the flammability limits. Detonation is a more energetic process that requires mixtures of hydrogen and oxidizer closer to stoichiometry; hence, the range of detonable concentrations is narrower than those for deflagration. The flame front of a deflagration, if adequately confined and subject to turbulence, can transition to a detonation.

2.9.2 Deflagration

Combustion often leads to flow of the burned and unburned gases. The flame speed, a function of the frame of reference, is a combination of the burning velocity (see Section 2.8.4) and the translational velocity of the bulk flow. In an isobaric system, the combustion of stoichiometric mixture of reactants, initially at NPT conditions, will yield an approximate eight-fold volume expansion. With confinement, this volume expansion can lead to acceleration of the flame speed. A flame front moving spherically outward relative to a stationary point has a flame speed three times the burning velocity. In a tube sealed at one end, a flame speed of nine times the burning velocity or 24 to 32 m/s (78.7 to 105 ft/s) can occur (Gugan 1979). If the flow becomes turbulent, increased mixing of reactants in the flame front can increase the rate of combustion and result in acceleration of flame speed to hundreds of meters per second.

2.9.3 Detonation

2.9.3.1 General

The worst-case event resulting from release of all forms of hydrogen into the ambient environment is mixing of the hydrogen with an oxidizer (usually air), and reaching concentrations that produce a detonation of the mixture. The positive buoyancy and rapid molecular diffusion of GH_2 means that any release will quickly mix with the surrounding gases. Rapid vaporization occurs and subsequent mixing with the surrounding gases can lead to a detonable mixture if LH_2 or SLH_2 spills or leaks. Should a detonation occur, the resulting reaction zone is a shock wave and the accompanying blast wave has much greater potential for causing personnel injury or equipment damage.

2.9.3.2 Detonation Limits

Lower and upper detonation limits vary considerably with the nature and dimensions of the confinement and cannot be specified for any fuel-oxidizer mixture unless the nature and dimensions of the confinement are also specified (Benz, Bishop, and Pedley 1988).

Figure A2.7 shows the minimum dimensions of hydrogen-air mixtures for detonation in three types of confinement at 101.3 kPa (14.7 psia). The figure shows a significant effect of confinement type on detonation limits. The ignition energy for detonation also becomes large for lean or rich mixtures;

however, it is possible to produce overdriven detonations when large ignition energy is introduced. Therefore, detonation limits found in the literature should be used with caution. Stable detonations are fairly well characterized by the Chapman-Jouget calculation. Table B.1 in Annex B gives the type of information obtained from such calculations for hydrogen-air. This table was produced using the Gordon-McBride computer code (Gordon and McBride 1994).

While values of lower and upper detonation limits for GH_2 -GOX of 15% and 90% hydrogen, respectively (Lewis and von Elbe 1961), are cited, the values suffer from the same shortcomings noted for hydrogenair and should be used with caution.

No specific detonation limits for LH₂ and air or GOX are available. The rapid volatilization of LH₂ to GH₂ and subsequent mixing with air or GOX would result in detonable mixtures as described above.

Mixtures of solid oxygen in excess (with respect to stoichiometry) and LH_2 is shock sensitive. A stimulus (shock) of 100 to 250 MPa (19,500 to 36,000 psia) will detonate such mixtures. For comparison, nitroglycerin is detonated by 250 to 500 MPa (36,000 to 73,000 psia) shocks (Perlee, Litchfield, and Zabetakis 1964).

2.9.3.3 Detonation Cell Size

A detonation wave is not a single planar wave front but has a three-dimensional structure consisting of cells. The size of the cell, as measured through the pattern left by a detonation on a smoked plate, is of considerable value in predicting the onset of detonation and describing the conditions for stable detonation waves. The cell size has been shown to relate to several key parameters in assessing a potential hazard, including critical energies and dimensional characteristics of structural confinement of the detonation (Lee et al. 1982). The length, *a*, of a detonation cell is one to two times its width, *b*. The aspect ratio, *a/b*, increases with decreasing initial pressure. Detonation cell lengths for stoichiometric GH₂-air/GOX at 101.3 kPa (14.7 psia) are 15.9 mm (0.626 in.) and 0.6 mm (0.024 in.), respectively (Bull, Ellsworth, and Shiff 1982). The measurements are specific to the system configuration used. Figure A2.8 gives the variation of detonation cell widths for GH₂-air mixtures at 101.3 kPa (14.7 psia). Ignition energy requirements depend on the concentration of the detonable mixture. Figure A2.9 gives the grams of tetryl required to detonate the GH₂-air mixtures shown in Figure A2.8.

2.9.3.4 Effect of Temperature, Pressure, and Diluents

The effect of temperature on detonation cell size for GH_2 -air mixtures gives mixed results. The original source should be consulted when citing such effects. Bull, Ellsworth, and Shiff (1982) showed decreasing cell size with increasing pressure for GH_2 -air. Increasing concentrations of diluents (% by volume CO_2 , or water (H_2O)) significantly increase cell widths of GH_2 -air detonations (Shepard and Roller 1982).

2.9.4 Deflagration-to-Detonation Transition

A hydrogen-air combustion can start as a detonation, or it can start as a deflagration and then transit to a detonation after the flame has traveled for some distance. The composition range in which a detonation can take place is narrower than that for deflagration. The commonly quoted range for detonation in a hydrogen-air mixture is from 18.3% to 59% hydrogen. However, with higher energy ignition sources, the limits can be extended. The factors that influence whether hydrogen-air combustion will occur as a detonation, rather than a deflagration, include the hydrogen percentage, the strength of the initiator, complete or partial confinement of the reaction, and the presence of structures that can induce turbulence in the flame front. An energetic source of initiation is required for combustion to start as a detonation. A mechanism to accelerate the flame velocity is necessary for a deflagration to transit to detonation. Factors that favor this transition include the composition being within the detonation range, a degree of confinement, and anything that can induce turbulence in the flame front as it travels through the combustible mixture. The latter tends to stretch out the flame front and increase its velocity (Lee 1977).

2.9.5 Energy of Explosion

The theoretical explosive yield for hydrogen-air is listed below for various forms and units:

- 1) NTP GH₂-air
 - a) Approximately 24 g trinitrotoluene (TNT)/g GH₂ (24 lb TNT/lb GH₂)
 - b) $2.02 \text{ kg TNT/m}^3 \text{ GH}_2 (0.126 \text{ lb TNT/ft}^3 \text{ GH}_2)$
 - c) 0.17 g TNT/kJ GH₂ (4 x 10⁻⁴ lb TNT/Btu GH₂)
- 2) NBP LH₂-air

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1.71 g TNT/cm<sup>3</sup> LH<sub>2</sub> (107.3 lb TNT/ft<sup>3</sup> LH<sub>2</sub>)
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It should be emphasized that only a fraction of this theoretical explosive yield will be realized in an actual open-air mishap. It is virtually impossible to spill or release a large quantity of fuel and have all of it mix in proper proportions with air before ignition. Example 1 in Annex B provides an example of the calculation of the detonation characteristics of hydrogen-air-oxygen mixtures using the Gordon-McBride computer code (Gordon and McBride 1994). TNT produces a short duration, high impulse pressure wave, whereas, a hydrogen-air explosion would have a longer duration and lower impulse pressure wave; the external effects of the two can be quite different.

2.10 Hydrogen Hazards

2.10.1 General

One of the major concerns in the use of hydrogen is that of an unwanted combustion (fire, deflagration, or detonation) because of hydrogen's properties such as its wide flammability range, low ignition energy, and flame speed. Other concerns include the interaction of hydrogen with materials that are in contact with it, such as hydrogen embrittlement of materials and the formation of hydrogen hydrides. The low temperature of liquid and slush hydrogen bring other concerns related to material compatibility and pressure control; this is especially important when dissimilar, adjoining materials are involved.

The hazards associated with the use of hydrogen can be characterized as:

- Chemical (ignition and burning)
- Physical (phase change, component failure, and embrittlement)
- Physiological (frostbite, respiratory ailment, and asphyxiation)

A combination of hazards occurs in most instances. The primary hazard associated with any form of hydrogen is inadvertently producing a flammable or detonable mixture, leading to a fire or detonation.

Safety will be improved when the designers and operational personnel are aware of the specific hazards associated with the handling and use of hydrogen. Hazards of hydrogen use are discussed in the following subsections of Section 2.10.

2.10.2 Accidents Involving Hydrogen

Accidents related to the use of hydrogen provide an excellent indication of the hazards involved in the use of hydrogen. Numerous industrial and aerospace accidents from the use of hydrogen have occurred as shown in Tables A7.1 through A7.3. Analyses of these accidents indicate the following factors are of primary importance in causing system failures:

- Mechanical failure of the containment vessel, piping, or auxiliary components (brittle failure, hydrogen embrittlement, or freeze-up)
- Reaction of the fluid with a contaminant (such as air in a hydrogen system)

- Failure of a safety device to operate properly
- Operational error

Fifty-three percent of the industrial accidents listed in Table A7.1 occurred because of leaks, off-gassing, and equipment ruptures. Fifteen percent were purging or vent-exhaust incidents, and the remaining 32% were other types of incidents. The vast majority of the accidents in ammonia plants listed in Table A7.2 occurred because of gaskets and valve packing leaking. Eighty of 96 aerospace hydrogen incidents listed in Table A7.3 involved release of GH₂ or LH₂. When accidents were not caused by equipment failure, they primarily occurred when procedures were not prescribed or when prescribed procedures were not followed (Ordin 1974). Accident reports showed that electrical short circuits and sparks were considered to be responsible for approximately 24% of the ignitions, and static charges were responsible for about 17% of the ignitions. Welding or cutting torches, metal fracture, gas impingement, and the rupture of safety disks were each considered responsible for 5% to 7% of the ignitions.

Analyses of accidents have shown that the response, through design or operating procedures, to a failure should be such that a single failure does not lead to a series of failures or a chain reaction of failures. That is, any failure must be restricted to a local event; otherwise, the hazard and probability for damage is greatly enhanced.

2.10.3 Common Hydrogen Hazards

Some common hydrogen hazards that are of concern in the use of hydrogen are discussed in the following subsections of 2.10.3.

2.10.3.1 Ignition

The ignition of GH_2 -air mixtures usually results in ordinary deflagration. The potential hazards are significantly less than if detonation results. It is possible that in a confined or partially confined enclosure a deflagration can evolve into a detonation. The geometry and flow conditions (turbulence) have a strong effect on the transition from deflagration to detonation.

Fires and explosions have occurred in various components of hydrogen systems as a result of a variety of ignition sources. Ignition sources have included mechanical sparks from rapidly closing valves, electrostatic discharges in ungrounded particulate filters, sparks from electrical equipment, welding and cutting operations, catalyst particles, and lightning strikes near the vent stack. Table A2.1 lists additional ignition sources.

Static electricity can generate sparks that will ignite hydrogen-air or hydrogen-oxygen mixtures. Static electricity is caused by many common articles, such as hair or fur when combed or stroked or a leather belt operating on a machine. People generate high-voltage charges of static electricity on themselves, especially when walking on synthetic carpet or dry ground, wearing nylon or other synthetic clothing, sliding on automobile seats, or combing their hair. Flowing GH₂ or LH₂ can generate charges of static electricity. This is true also for all nonconductive liquids or gases. Flow in SLH₂ has the potential for generating static electricity, although such an effect has not been confirmed. Turbulence in containers as well as laminar flow in systems has the same effect. Static charges may be induced during electrical storms (Beach 1964; Beach 1965).

Electrical sparks are caused by sudden electrical discharges between objects having different electrical potentials, such as breaking electrical circuits or discharges of static electricity. The sparks may dissipate tremendous amounts of energy in comparison with friction sparks.

Friction sparks are caused by hard objects coming into shearing contact with each other, such as metal striking metal, metal striking stone, or stone striking stone. Friction sparks are particles of burning material that have been sheared off as a result of contact. The particle initially is heated by the mechanical energy of friction and impact. Sparks struck by hand tools are considered to have low total energy. Mechanical tools such as drills and pneumatic chisels can generate high-energy sparks.

Impact sparks are also caused by hard objects coming into forcible contact with each other. Impact sparks are produced by impact on a quartzitic rock such as the sand in concrete. As with friction sparks, small particles of the impacted material are thrown off.

Objects at temperatures from 773 to 854 K (932 to 1,078 °F) can ignite hydrogen-air or hydrogen-oxygen mixtures at atmospheric pressure. Substantially cooler objects, about 590 K (602 °F), can cause ignition under prolonged contact at less than atmospheric pressure.

Open flames easily ignite hydrogen-air mixtures.

Provisions should be made to acceptably contain any resulting deflagration or detonation if ignition sources are a required part of a hydrogen use. As an example, a combustor or engine should not be operated in hydrogen-rich atmospheres without well-dispersed water sprays in its exhaust. Experience indicates that multiple bank sprays will partially suppress the detonation pressures and reduce the number and temperature of ignition sources in an exhaust system. Water sprays should not be relied on as a means of avoiding detonations. Carbon dioxide may be used with the water spray to further reduce hazards.

Ignition sources must be eliminated or safely isolated, but operations should be conducted as if unforeseen ignition sources exist or can occur.

2.10.3.2 Fire and Explosion

A potential fire hazard always exists when hydrogen is present.

GH₂ diffuses rapidly and air turbulence increases the rate of GH₂ dispersion. Evaporation can rapidly occur in an LH₂ spill, resulting in a flammable mixture forming over a considerable distance. Although ignition sources may not be present at the leak or spill location, fire could occur if the movement of the flammable mixture causes it to reach an ignition source.

Observation alone is not a reliable technique for detecting pure hydrogen-air fires or assessing their severity. An example of this is that of a fire resulted from an accident in which a small leak developed. The equipment was shutdown and the flame appeared to diminish; however, molten metal drippings from the equipment indicated a more severe fire was in progress.

A deflagration can result if a mixture within flammability limits is ignited at a single point.

A detonation can occur if a GH₂-air mixture is within detonability limits and an appropriate energy source is available. A deflagration can transform into a detonation if there is confinement or a mechanism for flame acceleration.

Flash fires or boiling liquid expanding vapor explosions (BLEVE) can occur when an external source of thermal energy heats LH₂ or SLH₂ and the containment vessel fails, allowing hydrogen to escape.

2.10.3.3 Leaks

Leaks can occur within a system or to the surroundings. Hazards can arise by air or contaminants leaking into a cold hydrogen system (LH₂ or SLH₂), such as by cryo-pumping. Leaks are usually caused by deformed seals or gaskets, valve misalignment, or failures of flanges or equipment. A leak may cause further failures of construction materials. For leaks involving LH₂, vaporization of cold vapor hydrogen to the atmosphere may provide a warning because moisture condenses and forms a fog. Undetected hydrogen leaks can lead to fires and explosions.

Hydrogen leaks generally originate from valves, flanges, diaphragms, gaskets, and various types of seals and fittings. The leaks usually are undetected because of the absence of a continuous hydrogen monitor in the area. An example of this condition was a large sphere partitioned by a neoprene diaphragm with hydrogen stored under the diaphragm and air above it. An explosion-proof fan was placed on top of the sphere to provide a slight positive pressure on the diaphragm. A violent explosion occurred in the sphere

after the plant was shutdown. Hydrogen leaked past the diaphragm when the fan was turned off. Ignition was attributed to an electrostatic discharge caused by motion of the diaphragm or a source associated with the explosion-proof fan. The explosion could have been avoided by using an inert gas instead of air across the diaphragm or monitoring the hydrogen concentration in the upper hemisphere.

2.10.3.4 Hydrogen Dispersion

A property of hydrogen that tends to limit the horizontal spread of combustible mixtures from a hydrogen spill is its buoyancy. Although saturated hydrogen is heavier than air at the temperatures existing after evaporation from a spill, it quickly becomes lighter than air, making the cloud positively buoyant. The dispersion of the cloud is affected by wind speed and wind direction and can be influenced by atmospheric turbulence and nearby structures. Although condensing moisture is an indication of cold hydrogen, the fog shape does not give an accurate description of the hydrogen cloud location (Witcofsky and Chirivella 1982).

The use of dikes or barricades around hydrogen storage facilities should be carefully examined because it is preferred to disperse any leaked or spilled LH₂ or SLH₂ as rapidly as possible. Dikes or berms generally should not be used unless their purpose is to limit or contain the spread of a liquid spill because of nearby buildings, ignition sources, etc. However, such confinement may delay the dispersion of any spilled liquid by limiting the evaporation rate, and could effect a combustion event that might occur.

2.10.3.5 Storage Vessel Failure

The release of GH_2 or LH_2 may result in ignition and combustion, causing fires and explosions. Damage may extend over considerably wider areas than the storage locations because of hydrogen cloud movement. Vessel failure may be started by material failure, excessive pressure caused by heat leak, or other failure mechanism.

2.10.3.6 Vent and Exhaust System

Vent and exhaust system accidents are attributed to inadequate ventilation and the inadvertent entry of air into the vent. Backflow of air can be prevented with suitable vent stack designs, provision of makeup air (or adequate supply of inert gas as the situation demands), check valves, or molecular seals.

2.10.3.7 Purging

Pipes and vessels should be purged with an inert gas before and after using hydrogen in the equipment. Nitrogen may be used if the temperature of the system is above 80 K (-316 °F), whereas, helium should be used if the temperature is below 80 K (-316 °F). Alternatively, a GH₂ flow may be used to warm the system to 80 K (-316 °F) and then switch to a nitrogen purge if the system is above 80 K (-316 °F); however, some condensation of the GH₂ may occur if the system contains LH₂. Residual pockets of hydrogen or the purge gas will remain in the enclosure if the purging rate, duration, or extent of mixing is too low. Tables A7.1 through A7.3 list 12 fire or explosion incidents that resulted from such situations, demonstrating the difficulties in purging hydrogen from large systems. Uniform mixing and dilution is unlikely in partially enclosed spaces. Reliable gas concentration measurements should be obtained at a number of different locations within the system for suitable purges.

An example of a dangerous purging practice that led to an explosion is that of purging only a portion of a hydrogen system that was isolated (supposedly) to reduce the purge time and volume. Complete isolation usually cannot be ensured because of the propensity of hydrogen to leak.

2.10.3.8 Vaporization System Failure

Pipe valving in vaporization systems may fail, causing injury from low-temperature exposures. Ignition of the hydrogen may occur, resulting in damage from fires and explosions.

2.10.3.9 Condensation of Air

An uninsulated line containing LH_2 or cold hydrogen gas, such as a vent line, can be sufficiently cold (less than 82 K (-312 °F) at 101.3 kPa (14.7 psia)) to condense air on the outside of the pipe. The condensed air, which can be enriched in oxygen to about 50%, must not be allowed to contact sensitive material or equipment. Materials not suitable for low temperatures, such as carbon steel, can become embrittled and fail. Moving parts and electronic equipment can be adversely affected. Condensed air must not be permitted to drip onto combustible materials such as tar and asphalt (an explosive mixture can be created).

2.10.3.10 Hydrogen Embrittlement

Containment systems may fail and the subsequent spills and leaks will create hazards when the mechanical properties of metallic and nonmetallic materials degrade from hydrogen embrittlement. Hydrogen embrittlement is a long term effect and occurs from continued use of a hydrogen system.

Tables A7.1 through A7.3 list piping and vessel ruptures caused by materials problems including hydrogen embrittlement, stress corrosion, and weld failures. Most of the damage was incurred by ignition of the hydrogen following the rupture. All repairs and modifications to piping and equipment that handles hydrogen must be carefully engineered and tested.

2.10.3.11 Physiological Hazards

4% by volume

Personnel present during leaks, fires, or explosions of hydrogen systems can incur several types of injury.

Asphyxiation is a hazard when someone enters a region where hydrogen or a purge gas has displaced the air, diluting the oxygen below 19.5% by volume. Stages of asphyxiation (at ground level) have been noted based on the oxygen concentration:

15% to 19% by volume	Decreased ability to perform tasks; may induce early symptoms in persons with heart, lung, or circulatory problems
12% to 15% by volume	Deeper respiration, faster pulse, poor coordination
10% to 12% by volume	Giddiness, poor judgment, slightly blue lips
8% to 10% by volume	Nausea, vomiting, unconsciousness, ashen face, fainting, mental failure
6% to 8% by volume	Death in 8 min; 50% death and 50% recovery with treatment in 6 min, 100% recovery with treatment in 4 to 5 min

Coma in 40 s, convulsions, respiration ceases, death.

Blast waves from explosions will cause injury as a result of overpressure at a given location or a combination of overpressure and duration at a given location as follows (DoD 6055.9):

3.4 psi overpressure	1% probability of eardrum rupture
15 psi overpressure	50% probability of eardrum rupture
74.4 psi overpressure	99% probability of eardrum rupture
15 psi overpressure for 100 ms duration, or 174 psi for 0.5 ms duration	Lung damage
50 psi overpressure for 79 ms duration, or 126 psi for 17 ms duration	Lethal Lung rupture

Permissible exposures to air-blast overpressures are given in DoD 6055.9-Std for various operations and conditions. Personnel shall be provided protection from potential blast overpressures when hazard assessments indicate the probability of an accidental explosion is above an acceptable risk level as determined by the AHJ (DoD 6055.9). This protection must limit incident blast overpressure to 2.3 psi (15.9 kPa) at an appropriate distance, which is determined on the basis of the mass of explosive involved (DoD 6055.9).

The **radiant heat** that reaches and is absorbed by a person from a GH₂-air flame is directly proportional to a variety of factors including exposure time, burning rate, heat of combustion, size of the burning surface, and atmospheric conditions (especially water vapor). Thermal radiation flux exposure levels show the following:

Flux of 0.47 W/cm² (1,490 Btu/min(ft²)) Pain felt in 15 to 30 s Skin burns in 30 s

Flux of 0.95 W/cm² (2,722 Btu/min(ft²)) Immediate skin reaction.

Figure A2.4 shows the distance-fuel weight relationship for third degree burns for thermal radiation of 134 J/m² (11.8 Btu/ft²). Figure A2.5 shows heat radiant intensity versus exposure time for threshold pain values. Figure A2.6 shows the effect of water vapor on radiant energy from a hydrogen fire.

Personnel shall be provided thermal protection when hazard assessments indicate the probability of an accidental explosion is above an acceptable risk level as determined by the AHJ. This protection must limit thermal flux exposure to 12.56 W/cm² (0.3 calories/cm²s) at an appropriate distance, which is determined on the basis of the mass of explosive involved (DoD 6055.9).

Cryogenic burns result from contact with cold fluids or cold vessel surfaces.

Exposure to large LH₂ spills could result in **hypothermia** if proper precautions are not taken.

2.10.3.12 Collisions During Transportation

Damage to hydrogen transportation systems (road, rail, air, and water) can cause spills and leaks that may result in fires and explosions.

Most of the incidents during transportation occurred outside of industrial facilities. Seventy-one percent of the hydrogen releases did not lead to an ignition. The relatively few ignitions may be due to a lack of ignition sources or the rapid dispersal of hydrogen into the atmosphere. In any event, the accident data provide further incentive to transport, transfer, and store hydrogen outdoors, away from occupied areas.

3 Materials for Hydrogen Service

3.1 Considerations for Materials Selection

3.1.1 General

Awareness of the unique properties of hydrogen and the effect of cryogenic temperatures on material behavior is essential for the safe use of hydrogen. A hydrogen system can consist of structural members, vacuum jackets, valve bodies and valve seats, electrical and thermal insulation, gaskets, seals, lubricants, and adhesives, and will involve a multitude of different materials. The appropriate data must be available for the selection of a material for a particular use. The selection of a suitable material for hydrogen applications requires consideration of the following as appropriate:

- Properties suitable for the design and operating conditions
- Compatibility with the operating environment
- Availability of selected material and appropriate test data for it
- Corrosion resistance
- Ease of fabrication, assembly, and inspection
- Consequences of a material failure
- Toxicity
- Hydrogen embrittlement
- Potential for exposure to high temperature from a hydrogen fire
- Cold embrittlement
- Thermal contraction
- · Property changes that occur at cryogenic temperatures

Many hydrogen material problems involve welds or the use of an improper material, such as a 400-series stainless steel for a pressure gage bourdon tube.

3.1.2 General Materials

A number of materials have been found acceptable for use in hydrogen service for conditions ranging from low temperature/low pressure to high temperature/high pressure. Table A5.1 gives a summary of the compatibility of some materials for hydrogen service. Table A5.2 gives a selection of materials for many typical applications. The selection of a material depends on the specific conditions of operation. The tables are provided as guidelines.

3.1.3 Metallic Materials

Metals with a face-centered cubic structure, such as austenitic stainless steels, aluminum alloys, copper, and copper alloys, generally are satisfactory for hydrogen service. Nickel, a face-centered cubic material, is an exception and generally is not used because it is subject to severe hydrogen embrittlement. Unstabilized austenitic stainless steel (some of the 300 series) can revert to a martensitic structure when stressed above the yield stress at low temperature, reducing the ductility of the steel. Ordinary carbon steels may be used in GH₂ service, but they lose their ductility at LH₂ temperatures and are considered too brittle for low-temperature service. Iron, low alloy steels, chromium, molybdenum, niobium, zinc, and most body-centered cubic crystal structure metals are not acceptable for use at cryogenic temperatures. The

yield and tensile strength of metals with a body-centered cubic structure depend to a great extent on the temperature, and if the materials exhibit a substantial loss of ductility within a narrow temperature range.

Trapping sites have been identified in face-centered cubic metals and alloys; therefore, these materials should be evaluated carefully in making selections. Trapping is pronounced at low temperatures. It is important in the temperature region where hydrogen embrittlement is most pronounced. Trapping is not important in short-time GH₂ or LH₂ exposure.

The designation that a material is suitable for cryogenic service does not necessarily indicate that the material is suitable for LH₂ or SLH₂ service. Nickel steels with 3.5, 5, and 9% nickel are considered satisfactory for cryogenic service with specific minimum temperature limits as follows:

- 190 K (-150 °F) for 3.5-nickel steel
- 129 K (-260 °F) for 5-nickel steel
- 76 K (-323 °F) for 9-nickel steel

3.1.4 Nonmetallic Materials

Tables A5.1 and A5.2 list some nonmetallic materials that may be used in hydrogen service. The use of elastomers and plastics should be limited in gasketing, packing, or other sealing elements in which failure as a result of fire could cause hydrogen leakage.

The valve seat materials should be the materials of standard industrial practice for GH₂ near room temperature (Moore et al. 1959).

TeflonTM (or the equivalent) or polychlorotrifluoroethylene (PCTFE) can be used in cold GH_2 or LH_2 systems for the following:

- Valve seats (modified Teflon™, although Fluorogreen™ is preferred, or the equivalent)
- Soft coatings on metallic O-rings to provide more positive seals
- · Flat, thin gaskets for tongue and groove flanges in which the gasket is shrouded on four sides
- Spacers in the vacuum area between liquid, the flow tube, and vacuum pipe
- Gland packing or seals (only if maintained near ambient temperature as in an extended bonnet of a shutoff valve).

All Teflon[™] (or the equivalent) gaskets must be captured on all sides to prevent cold flow and subsequent leakage. The contraction or shrinkage allows leakage when Teflon is cooled from ambient to cryogenic temperatures. Filled Teflon materials, or PCTFE, are preferred to Teflon[™] (or the equivalent) for use in LH₂ service. PCTFE has a higher tensile strength and is less brittle at cryogenic temperatures than Teflon[™] (or the equivalent). Valves for liquid service over 2.1 MPa (300 psia) should use metal-to-metal seats because the pressure requires excessive seating force for the PCTFE and Teflon[™] (or the equivalent) (Moore et al. 1959)

3.1.5 Clad Materials

The base metal for a component should be an acceptable material when a clad or lined component is used. The thickness used in pressure design should not include the thickness of the clad or lining. The allowable stress used should be that for the base metal at the design temperature. Clad components may be difficult to weld.

3.1.6 Gasket Materials

Table A5.2 lists some gasket materials satisfactory for hydrogen service.

3.1.7 Welds

Welds are susceptible to hydrogen embrittlement in all hydrogen environments. The heat-affected weld zone frequently produces hard spots, residual stresses, and a microstructure conducive to embrittlement. Post-weld annealing may be required to restore a favorable microstructure. Test programs with type 301 stainless steel and InconelTM 718 (or the equivalent) have shown that flaw growth in LH₂ or SLH₂ storage systems is considerably greater in the welds than in the parent metal. Type 347 stainless steel is very sensitive to cracking during welding and should not be used without taking proper welding precautions. Welding requirements are given in the ASME BPVC and ASME B31.3.

3.1.8 Material Properties

It generally is best to use room temperature (or higher temperature if necessary) for operational requirements and strength of a material in the design of cryogenic equipment, although the strength of materials generally tends to increase as their temperature is lowered. This recommendation is based on the recognition that cryogenic equipment must also operate at room temperature (or higher), and temperature gradients are possible within the equipment. Many test conditions and the form of the material (such as plate, bar, wire, pipe, forgings, etc.) affect material properties; consequently, unless the conditions and forms are given and are applicable, material property values should not be considered as approved design values. Approved design values may be obtained, for example, from ASME BPVC that gives allowable stresses for materials used in pressure vessels. Table A5.3 presents the allowable stress for some representative materials from the ASME B31.3. Tables A5.4 (elastic properties), A5.5 (mechanical properties), and A5.6 (thermal properties) give some typical property values at room temperature and LH₂ temperature for some materials suitable for LH₂ service.

The effect of exposure to hydrogen should be considered in setting the allowable stress for hydrogen systems. Often, the allowable stress for vessels or piping used for GH₂, LH₂, and SLH₂ is set at no greater than 50% of the minimum yield of the material at ambient temperature as an added safety factor.

3.1.9 Forbidden Materials

Gray, ductile, or cast iron shall not be used in hydrogen service (29 CFR 1910.103; NFPA 50A).

Asbestos and asbestos impregnated with Teflon™ (or the equivalent) were once recommended for hydrogen service, but they shall not be used because of the carcinogenic hazard of asbestos.

3.1.10 Quality Control

Materials for hydrogen service should be carefully selected, and good quality control procedures should be used. A material shall not be used until appropriate testing and analysis have indicated that the material is satisfactory for its intended purpose if it is not known to be compatible with hydrogen. Materials used shall be compatible with GH₂, LH₂, and SLH₂ under the conditions (such as temperature and pressure) in which they will be used and shall conform to the specifications approved by the responsible engineering authority. The properties used for design should be based on tests conducted under conditions that simulate service or worst-case conditions. Test techniques to investigate material compatibility with hydrogen should include the direct exposure of the materials. As appropriate, testing should include tensile, fracture toughness, crack growth, fatigue (including low-cycle fatigue), bend, and stress rupture over a range of pressures and temperatures. Only materials that have been evaluated for suitable fatigue life should be used because LH₂ or SLH₂ systems are subjected to cyclic loading. Materials for hydrogen systems should be selected after evaluations under interactions of stress, pressure, temperature, and exposure conditions.

The designer should be careful in selecting material property values reported in the literature because test and material conditions are highly variable.

3.2 Hydrogen Embrittlement

3.2.1 General

Hydrogen can cause a significant deterioration in the mechanical properties of metals. This effect is referred to as hydrogen embrittlement. Hydrogen embrittlement involves a large number of variables such as the temperature and pressure of the environment; the purity, concentration, and exposure time of the hydrogen; and the stress state, physical and mechanical properties, microstructure, surface conditions, and nature of the crack front of the material.

3.2.2 Types of Embrittlement

Hydrogen embrittlement can occur in one or a combination of the following three forms:

- 1) Environmental hydrogen embrittlement that has been observed in metals and alloys plastically deformed in a GH₂ environment. Deformations under such conditions lead to increased surface cracks, losses in ductility, and decreases in fracture stress. Cracks start at the surface.
- 2) Internal hydrogen embrittlement caused by absorbed hydrogen. Small amounts of hydrogen may cause premature failures in some metals; the failures may occur with little or no warning. Cracks start internally.
- 3) Hydrogen reaction embrittlement that occurs when the absorbed hydrogen chemically combines with one or more of the constituents of the metal to form a brittle hydride. This reaction occurs more readily at elevated temperatures. Hydrogen has formed methane with the carbon in steels.

Table A5.7 gives some of the characteristics of these embrittlement forms. Tables A5.8 and A5.9 list additional information on the embrittlement of materials. Table A5.8 summarizes the susceptibility of some materials to embrittlement in hydrogen at a 68.9 MPa (10,000 psi) and 295 K (72 °F). Table A5.9 gives the effects of exposure to air, helium, and hydrogen at various pressures on the yield strength, ultimate strength, and ductility of some aluminum alloys, nickel, nickel alloys, and copper alloys.

3.2.3 Effect on Mechanical Properties

The mechanical properties of metals are reduced in the presence of hydrogen. Tables A5.8 and A5.9 give selected data for hydrogen effects on several metals and alloys. Studies indicate the following:

- The susceptibility of an alloy to adverse hydrogen effects increases as the strength of the alloy increases.
- Hydrogen embrittlement has been observed over a wide range of temperatures, but for many metals and alloys, the effect of internal and environmental hydrogen embrittlement is maximum in the temperature range of 200 to 300 K (-100 to 80 °F) (Swisher et al. 1974). In contrast, hydrogen reaction embrittlement is associated with higher temperatures, such as above room temperature.
- The susceptibility of steel to hydrogen embrittlement increases as the hydrogen purity increases.
- Susceptibility to embrittlement generally increases as the tensile stress level increases.
- Embrittlement leading to an increased crack growth rate results in a decreased fatigue life.

3.2.4 Surface and Surface Films

The hydrogen compatibility of metastable austenitic stainless steels such as American Iron and Steel Institute (AISI) type 304 is markedly influenced by surface finish.

Severe ductility losses and extensive surface cracking have been observed in as-machined samples with a 64 rms finish tested to failure in 69 MPa (10,000 psi) hydrogen. The extent of cracking could be minimized by removing the layer produced by machining.

Oxides probably are the most common form of surface film on metals and alloys. Fabrication and operation of engineering structures can lead to formation or growth of oxides. Oxides restrict hydrogen absorption and may influence the degree of embrittlement in any given exposure because oxides usually have a lower permeability than the base metals. Anomalies in the absorption and permeation of hydrogen in InconelTM (or the equivalent), austenitic stainless steels, aluminum alloys, copper, and low-alloy steels have been attributed to the oxide films.

Synthetic surface films must be ductile at their operating temperature. Copper and gold are recommended.**

3.2.5 Effect of Electrical Discharge Machining

The potential for hydrogen embrittlement is increased by electrical discharge machining. Electrical discharge machining is a commonly used technique for producing holes, notches, slots, or other cavities in electrically conductive material. Electrical discharge machining processes can introduce hydrogen into a machined component. Hydrogen is provided by the dielectric fluid (usually oil or kerosene) when it is ionized by the electrical discharge.

3.2.6 Effect of Trapping Sites

An additional concern is that of trapping hydrogen at sites within the structure of the metal, including dislocations, grain and phase boundaries, interstitial or vacancy clusters, voids or gas bubbles, oxygen or oxide inclusions, carbide particles, and other lattice defects. Hydrogen can be trapped at these sites because such defects occur in most metals. Trapping is most pronounced at low temperatures and is important in the near-room temperature region where hydrogen embrittlement is also pronounced.

3.2.7 Reducing the Effects of Hydrogen Embrittlement

Hydrogen-induced losses in mechanical properties have been attributed to three independent primary factors:

- The development of a critical, absorbed, localized hydrogen concentration
- The existence of a critical stress intensity (crack length and applied or residual stress)
- The existence of a susceptible path for hydrogen damage

Successful loss prevention measures include coatings, elimination of stress concentrations, impurity additions to gas-phase hydrogen, oxidation treatments, proper grain size or grain size mix, specifications of inclusion morphology, and careful alloy selection. Some suggestions for addressing hydrogen embrittlement concerns include the following:

- Aluminum is one of the few metals known to show only minimal susceptibility to hydrogen, so its use effectively eliminates hydrogen embrittlement.
- Most GH₂ equipment is made of medium strength steel and most LH₂ equipment is made of stainless steel. Hydrogen embrittlement concerns are addressed through increased thickness, surface finish, welding techniques, and materials selection.
- Containers with thick walls of low-strength metals will generally contain hydrogen more safely than containers fabricated from similar alloys treated for high strength, subject to appropriate welding techniques.

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^{**} McPherson, W. B. Private Communication (1995).

- A metal or alloy is almost certain to have a lower resistance to fatigue than if hydrogen were not present if it is exposed to hydrogen and cyclic stresses. Designers should, in the absence of data, assume a substantial (up to fivefold) decrease in resistance to fatigue.
- Avoid the use of body-centered cubic metals and alloys whenever practical. Cast iron shall not be used.
- Hydride-forming metals and alloys should not be used as structural materials for hydrogen service.
 Their use requires careful consideration of operating temperatures and adverse effects of hydride formation.
- Exposure temperatures below room temperature generally retard hydrogen reaction embrittlement; however, environmental and internal hydrogen embrittlement are increased in the temperature range of 200 to 300 K (-100 to 80 °F).

3.3 Thermal Considerations in Material Selection

3.3.1 Low-Temperature Mechanical Properties

The selection of a structural material for use in LH_2 or SLH_2 service is based primarily on the mechanical properties (such as yield and tensile strength, ductility, impact strength, and notch insensitivity) of the material. The material must have certain minimum values of these properties over the entire temperature range of operation, with appropriate consideration for nonoperational conditions such as a hydrogen fire. The material must be metallurgically stable so phase changes in the crystalline structure do not occur with time or repeated thermal cycling.

Three main categories of material behavior to be considered are the following:

- 1) The transition from ductile to brittle behavior as a function of temperature
- 2) The modes of plastic deformation, particularly certain unconventional modes encountered at very low temperatures
- 3) The effect of metallurgical instability and phase transformations in the crystalline structure on mechanical and elastic properties

Two thermal properties to be considered in the selection of a material for LH₂ and SLH₂ service are low-temperature embrittlement and thermal contraction, which are discussed below.

3.3.2 Low-Temperature Embrittlement

Some materials change from ductile to brittle behavior as their temperature is lowered. This temperature varies for different materials and can be much higher than cryogenic temperatures.

The failure of a liquefied natural gas (LNG) storage vessel in Cleveland in 1944 is an example of low-temperature embrittlement and of the tragic consequences of a low-temperature embrittlement failure. An LNG storage vessel made of 3.5% nickel steel with a capacity of 4,248 m³ (150,000 ft³) ruptured and released 4,163 m³ (147,000 ft³) of LNG. The LNG ignited after having spread into nearby storm sewers. A nearby storage vessel of a different design collapsed from the fire and spilled its contents, which also burned. Flames were reported to have extended to a height of at least 2,800 ft (853 m). The result was 200 to 400 injuries and 128 deaths and an estimated \$6.8 million (1944 dollars) in property damage (Zabetakis 1967).

The Charpy impact test is commonly used to determine the ductility of a material (Edeskuty and Stewart 1996). Figure A5.1 shows the results of the Charpy impact test at various temperatures for several materials. The figure clearly shows the ductile-to-brittle transition of C1020 carbon steel and 201 stainless steel. The large decrease in the Charpy impact strength for the 9% nickel steel indicates it is unsatisfactory for LH₂ service. In contrast, the Charpy impact strength for 304 stainless steel does not show a significant change, it actually increases slightly as the temperature decreases, indicating

304 stainless steel can be used for LH₂ service. The Charpy impact strength of 2024-T4 aluminum is low, but does not change much as the temperature decreases, indicating that it can be used for LH₂ service but with caution because of its low value.

Another indication of the ductile or brittle behavior of a material is given by the relationship of the yield and tensile strengths of the material as a function of temperature. The yield and tensile strengths of a material generally increase as the temperature decreases, but the rate of increase of the two properties gives an indication of the change in ductility of the material. Figure A5.2 shows the yield and tensile strengths of 5086 aluminum (a material considered satisfactory for LH₂ service) as a function of temperature. The figure shows that the tensile strength increases faster than the yield strength as the temperature decreases. The distance between the two curves provides an indication of the ductility of the material, and in this case, it indicates the material remains ductile. In contrast, Figure A5.3 shows the behavior of AISI 430 stainless steel, a material that becomes brittle. The two curves for AISI 430 stainless steel approach each other at liquefied nitrogen (LN₂) temperature, 77 K (-320 °F); therefore, the material becomes increasingly brittle as the temperature decreases and it is not considered satisfactory for cryogenic service (McClintock and Gibbons 1960).

3.3.3 Thermal Contraction

Materials generally have a positive thermal expansion coefficient (although there are a few exceptions to this over limited temperature spans). The temperature span from ambient to cryogenic temperature is about 200 K (360 °F) or more. Such a large temperature decrease will result in a significant thermal contraction in most materials, and this contraction must be accommodated in the use of the material at cryogenic temperatures. Figure A5.4 shows (using copper for example) that the thermal expansion coefficient of a material is itself a function of temperature.

About 90% of the total contraction from room temperature, 300 K (80 °F), to a temperature lower than LN_2 temperature, 77 K (-320 °F), will have occurred by a temperature of 77 K because of the decrease in the thermal expansion coefficient as a function of temperature for most materials. Figure A5.5 shows that a thermal contraction of about 0.3% in iron-based alloys, slightly over 0.4% in aluminum, and well over 1% in many plastics occurs in cooling from room temperature to cryogenic temperature. These values can be used for estimates. Figure A5.5 shows, for several materials, the total integrated thermal contraction from room temperature to lower temperatures.

4 Hydrogen Facilities

4.1 Safety Policy

4.1.1 General

The safe and successful use of hydrogen starts with knowing and adhering to appropriate standards and guidelines for the design of the facilities.

Safety shall be considered in all phases of a hydrogen facility life cycle, beginning with its initial design and continuing through its fabrication, construction, operation, and maintenance, and ending with its decommissioning.

The safe operation of a hydrogen system depends on a facility with the necessary safety features designed and built into it and operating personnel appropriately trained in and cognizant of safety.

The safety of the design shall be reviewed in accordance with policy established by the AHJ before hydrogen facilities, equipment, and systems are constructed, fabricated, and installed. Safety review and concurrence procedures should include intended personnel operations. Construction and construction practices shall be in accordance with 29 CFR 1926.

4.1.2 Installation Pressure Systems Manager

This Guide recommends that a qualified person be designated to direct technical efforts; approve pressure vessels and pressurized systems (including vacuum) designs, repairs, configuration changes, etc.; and act as the primary point of contact for all recertification activities (National Aeronautics and Space Administration (NASA) NPD 8710.5 2003). In larger organization this person would be known as the Installation Pressure Systems Manager and would report to a Pressure Systems committee. Where appropriate, the committee should conduct reviews, recommend requirements and procedures, maintain an overview of pressure system technology, participate in recertification activities, and provide guidance on pressure system safety to appropriate officials including the Pressure Systems Manager and safety officials.

4.1.3 Fire Protection

Conventional fire protection doctrine and existing codes and standards may not be appropriate in some cases. For example, as a result of the unique nature of NASA's mission, a number of specialized facilities and operations are required by NASA. Nevertheless, adequate safeguards shall be provided for all facilities and operations.

An analysis shall be conducted to identify all fire hazards and accomplish the following:

- Significant hazards shall be eliminated or reduced to acceptable risk levels.
- Where the hazard cannot be eliminated or reduced, the system components associated with the hazard shall be relocated to an area less threatening to people and property as directed by the AHJ.
- Where the hazard cannot be eliminated, reduced, or removed, the system components associated with the hazard shall be isolated within the facility so as not to pose a danger to the remainder of the structure or its occupants.
- Where the hazard cannot be eliminated, reduced, relocated, or isolated, protection shall be provided
 to ensure adequate levels of human and structural safety. Should a fire occur, the occupants of the
 facility shall be provided with protection to enable them to leave the area safely and the structure will
 be protected to ensure its continued integrity.

4.2 Safety Reviews

All hydrogen activities, both large and small, should be subject to safety reviews. At each phase in the activity life cycle, specific safety tasks shall be accomplished to ensure safety during construction, operation, maintenance, and final disposition of the facility. Safety tasks identified in the Safety Management Plan for each facility acquisition should be tailored to include the appropriate tasks considering the size and complexity of the project and the associated safety risks. Section 4.2 describes recommended safety tasks for new facilities and for modification and/or rehabilitation of existing hydrogen facilities.

4.2.1 New Facilities

Safety assessment shall be integrated into the overall facility design review of major projects. Each design review phase shall address and evaluate the safety aspects of the project consonant with its level and maturity. Reviews shall be conducted as appropriate, and will include the following:

- Concept design review (10% Review). Purpose and design performance criteria should be
 established. Proposed and selected design approaches and basic technologies should be delineated
 sufficiently to indicate the type and magnitude of the principal potential hazards. Applicable design
 codes, safety factors, and safety criteria should be specified. A preliminary hazards analysis shall be
 started. Appropriate safety tasks should be planned and become the foundation for safety efforts
 during the system design, manufacture, test, and operations.
- **Preliminary design review** (30/60% Review). Stress calculations for critical structures shall show that design codes, safety factors, and safety criteria have been met. The preliminary hazards analysis shall be completed; system/subsystem hazards analyses should be under way.
- Critical design review (90% Review). The design shall be reviewed for conformance to design
 codes, required safety factors, and other safety criteria. Proposed construction methods and
 arrangements shall make clear that construction hazards will be effectively controlled. Procurement
 documents, such as a statement of work (SOW) shall specify appropriate safety requirements. The
 system/subsystem hazards analyses shall be completed and close-out actions shall be proceeding.
 An operational hazards analyses shall be under way.
- **Design certification review** (100% Review). All project documentation (such as drawings, SOWs, and specifications) should be completed, reviewed, and approved. All hazards analyses shall be completed, including close-out actions. Actions from previous reviews should be verified as complete.
- Ongoing system/subsystem hazards analyses. Hazards and operational analyses will be updated during operations and testing.
- Review of procedures and equipment (test readiness review). Operational procedures, along with instrumentation and control systems, shall be evaluated for their capacity to provide the required safety. Equipment performance should be verified by analysis or certification testing as directed by the AHJ. It may be necessary to develop special procedures to counter hazardous conditions.
- Emergency procedures review. The safety of personnel at or near hydrogen systems should be carefully reviewed and emergency procedures developed in the earliest planning and design stages. Advance planning for a variety of emergencies such as fires and explosions should be undertaken so the first priority is to reduce any risk to life.
- Review of operations (operational readiness review). A review of operations may be required for any major facility change. Hydrogen hazards should be reviewed for compliance with directives by the AHJ.

4.2.2 Existing Facility Modification or Rehabilitation

For minor modifications to, or rehabilitation of, existing hydrogen systems, the safety review process should provide review stages that include the following:

- Preliminary design and layout. The initial request shall include a hazards analysis using the appropriate tools and equipment, such as: failure modes and effects analysis, fault tree analysis, sneak circuit analysis, event tree analysis, and hazard operability study for the safety task undertaken. This hazard analysis shall identify all of the hazards associated with the facility or operations from the beginning of hydrogen use to the disposal of the hydrogen. Consideration should be given in the design review and hazards analysis for the shutdown of transfer systems, for the automatic closing of special lines and systems, and for the use of isolation valves in various legs of multiple systems.
- **Final design**. Review of the final drawings, designs, structures, and flow and containment systems shall include a safety assessment review. Assessment reviews shall identify areas of compliance as required by local, state, and federal agencies.

4.2.3 Safety Assessment Review

The Safety Assessment Review shall be updated anytime a system or process is changed. An annual facility inspection shall be conducted and documented. A formal operating and support hazard analysis shall be performed as directed by the AHJ. Significant hazards identified shall be eliminated or reduced to acceptable risk levels. Record of inspections and operating and support hazard analyses shall be retained on file at the involved installation for a period of time as specified by the AHJ.

4.2.4 Operating Procedures

Operating procedures, along with instrumentation and control systems, shall be evaluated for their capacity to provide the required safety. Equipment performance shall be verified by analysis or certification testing.

4.2.5 Training

Operator training shall be reviewed and demonstrated to be adequate before operations commence. Operator training shall be evaluated continuously (29 CFR 1910.1200).

4.2.6 Emergency Procedures

The safety of personnel at and near a hydrogen facility shall be carefully reviewed and emergency procedures developed at the earliest planning and design stages. Advance planning for a variety of emergencies such as fires and explosions shall be undertaken so the first priority is the reduction of risk to life.

4.3 General Facility Guidelines

The facility and structure design should include sufficient details for demonstrating satisfactory safety in the storage and transfer areas. The facility design should provide for good illumination, lightning protection, alarm systems, and gas detection and sampling systems. As delineated in Section 1.1, separate standards and guidelines address different portions of overall hydrogen systems; however, there are safety considerations for the design of facilities common to all portions or subsystems.

4.3.1 Electrical Considerations

The requirements for electrical equipment and wiring that are used in or near a hydrogen system or storage vessel are determined and classified depending on 1) the properties of the flammable or combustible liquids, gases, or dusts that may be present, and 2) the probability that a flammable or combustible mixture or quantity is present (29 CFR 1910.307). Class I locations are those in which flammable gases or vapors are, or may be, present in the air in quantities sufficient to produce explosive

or ignitable mixtures (29 CFR 1910.399). Class I locations are classified as either Division 1 or Division 2 locations as described below. Hazardous gases, vapors, and dusts are defined by "Groups" as characterized by their ignitable or combustible properties in NFPA 70 (29 CFR 1910.307). Hydrogen is included in Group B in NFPA 70.

Class I, Group B, Division 1

A region is classified as a Class I, Group B, Division 1 location (29 CFR 1910.399) if a flammable hydrogen mixture may exist in the following circumstances:

- Under normal operating conditions
- Because of frequent system repairs, maintenance operations, or leakage
- As a result of breakdown or faulty operation of equipment or processes that might also cause simultaneous failure of electrical equipment

An example of a Class I, Group B, Division 1 location is the place where LH₂ is transferred from one container to another (29 CFR 1910.399).

Class I, Group B, Division 2

A region is classified as a Class I, Group B, Division 2 location (29 CFR 1910.399) if:

- Hydrogen is handled, processed, or used, but the hydrogen is normally confined within a closed container or closed system from which it can escape only in case of accidental rupture or breakdown of the container or system, or in case of abnormal operation of the equipment.
- Formation of a flammable hydrogen mixture is normally prevented by positive mechanical ventilation which might become combustible through failure or abnormal operations of the ventilating equipment.
- It is adjacent to a Class I, Group B, Division 1 location, and if a flammable mixture may occasionally be communicated unless such communication is prevented by adequate positive-pressure ventilation from a source of clean air, and effective safeguards against ventilation failure are provided.

NFPA 70 requires that meters, instruments, and relays, including kilowatt-hour meters, instrument transformers, resistors, rectifiers, and thermionic tubes in Class I Division 1 locations be provided with enclosures approved for Class I Division 1 locations. Enclosures approved for Class I Division 1 locations include: 1) explosion-proof enclosures, and 2) purged and pressurized enclosures.

An explosion-proof enclosure is a case that is capable of (29 CFR 1910.399):

- Withstanding an explosion of a specified gas or vapor that may occur within it.
- Preventing the ignition of a specified gas or vapor surrounding the enclosure by sparks, flashes, or explosion of the gas or vapor within it.
- Operating at such an external temperature that it will not ignite a surrounding flammable atmosphere.

Explosion-proof does not mean that the case must be gas tight.

A Division 1 installation differs from a Division 2 installation mainly in its degree of isolation from the ignition sources that may occur in the electrical system. A Division 1 installation relies heavily on explosion-proof enclosures.

Requirements for electrical equipment and wiring in locations that are classified (e.g., Class 1, Division 1) are given in 29 CFR 1910.307 and NFPA 70.

Equipment, wiring methods, and installations of equipment in hazardous (classified) locations shall be: 1) intrinsically safe, 2) approved for the hazardous (classified) location, or 3) safe for the hazardous (classified) location. Requirements for each of these three options are given in 29 CFR 1910.307.

NFPA 70 contains guidelines for determining the type and design of equipment and installations that will be the requirements for the class, group, and division locations (29 CFR 1910.307.

All conduits shall be threaded and shall be made wrench-tight. Where it is impractical to make a threaded joint tight, a bonding jumper shall be utilized (29 CFR 1910.307). Electrical conduits and their associated enclosures separated from hydrogen by a single seal or barrier are classed as a Division 2 location if the environment outside of the conduit and enclosures is a nonhazardous location (29 CFR 1910.399).

Equipment that has been approved for a Division 1 location may be installed in a Division 2 location of the same class and group. General purpose equipment or equipment in general-purpose enclosures may be installed in Division 2 locations if the equipment does not constitute a source of ignition under normal operating conditions (29 CFR 1910.307).

All electrical sources of ignition should be prohibited in classified areas, including open electrical arcing devices and heaters or other equipment that operate at elevated temperatures. This means using approved explosion-proof equipment (Class 1, Group B, Division 1) or selecting non-arcing equipment approved for Division 2 (NFPA 70).

Intrinsically safe installations in accordance with NFPA 70 and ANSI UL913 may be used. The intrinsically safe installation should be approved for hydrogen service.

When properly classified equipment is not available, general-purpose equipment in general-purpose housing may be used if it is continuously pressure purged with clean air or nitrogen provided no ${\rm GH_2}$ sources are plumbed into them. Positive indication of continued purge shall be provided. The purge system shall be in compliance with NFPA 496 and 29 CFR 1910.103. The cost of an installation will be reduced and safety increased if the items that might become ignition sources are located outside the hazardous area. Also, systems installed in the hazardous area, but not required during hazardous periods, may be built with general-purpose equipment provided they are disconnected before the hazardous period begins. The conduits for such systems must be sealed in accordance with NFPA 70 when they leave the hazardous area.

4.3.2 Bonding and Grounding

Mobile hydrogen supply units shall be electrically bonded to the system before discharging hydrogen (NFPA 50A; 29 CFR 1910.103).

Static and mobile LH₂ containers and associated piping shall be electrically bonded and grounded (NFPA 50B; 29 CFR 1910.103).

NFPA 70 defines the terms "bonded" and "grounded" and lists sizes of grounding conductors and acceptable connections based on the expected amperage to ground.

All off-loading facilities shall provide easily accessible grounding connections and be located outside the immediate transfer area. Facility grounding connections should be less than 10 Ω resistance. Transfer subsystem components should be grounded before subsystems are connected.

Electrical wiring and equipment located within 0.9 m (3 ft) of a point at which connections are regularly made and disconnected shall be in accordance with NFPA 70 for Class I, Group B, Division 1 locations.

4.3.3 Roadways and Area Surfaces

The roadways and area surfaces located below LH₂ piping from which liquid air (see Sections 2.6.3 and 2.10.3.9) may drop shall be constructed of noncombustible materials (NFPA 50B) such as concrete or crushed stone. Uninsulated piping and equipment that can be at LH2 temperature shall not be installed

above asphalt surfaces or other combustible materials that are not compatible with the oxygen-enriched liquid resulting from cooling and condensing air (CGA G-5.4). Asphalt, a common paving material, can become combustible and can even react explosively as a result of liquid air falling on it. For the same reason, organic and combustible materials (including debris and trash) should not be permitted underneath a surface from which liquid air may drip.

4.3.4 Transfer Piping

Piping carrying hydrogen to the use point from the dewars, trailers, and storage vessels shall be installed above ground. Lines crossing roadways should be installed in concrete channels covered with an open grating. Hydrogen transmission lines shall not be located beneath electric power transmission lines (29 CFR 1910.103) and in general should be located as far away as possible from other lines, process equipment, and hazardous fluids (CGA G-5.4). Installation of powered systems, electrical equipment, and wiring in proximity to hydrogen piping shall be in accordance with NFPA 70.

The hazard involved in a buried pipe is illustrated by an explosion that occurred in one of the buildings of a test stand complex. The explosion resulted when galvanic corrosion and high pressure caused a GH₂ leak in an underground pipe. GH₂ was trapped under the test stand apron and entered several rooms. The explosion originated in the basement. Shock waves traveled through connecting ducts to a second room, causing a second explosion.

4.3.5 Elimination of Ignition Sources

There shall be no sources of ignition, such as open flames, electrical equipment, or heating equipment in buildings or special room containing hydrogen systems (29 CFR 1910.103; NFPA 50A and 50B).

Ignition sources must be eliminated or safely isolated and operations should be conducted as if unforeseen ignition sources exist or can occur.

4.3.5.1 Lightning Protection

Lightning protection in the form of lightning rods, aerial cable, and ground rods suitably connected should be provided at all preparation, storage, and use areas. All equipment in buildings should be interconnected and grounded to prevent inducing sparks between equipment during lightning strikes. The design of lightning protection systems shall be in accordance with requirements of NFPA 780.

4.3.5.2 Static Charge in Flowing Fluid

Strong static charges may be generated in flowing fluids containing solid or liquid particles in spite of all precautions. The sources may be unknown but could be caused by the rapid movement of particles in pipes or vessels during transfer. Sufficiently high potentials can be developed that will discharge as a spark. Vents or other locations where static buildup can occur should be adequately grounded. Vents should be directed to avoid impingement on piping or structures not adequately grounded, as they may buildup charge (see following section).

4.3.5.3 Vent Stack Discharge Rod

A discharge rod may be used to dissipate static charge buildup associated with high velocity venting where ignition of the vented GH_2 is a concern. The discharge rod, welded to the vent, should be extended above the gas discharge point so normal venting GH_2 is always below the flammability point at the discharge rod tip for systems with static vent stacks.

4.3.5.4 Limiting Spark Generation

The following measures should be taken to limit spark generation potential:

- Bond and ground all metal parts of a test rig and the structure enclosing it.
- Use conductive machinery belts.

- Personnel shall ground themselves before touching or using a tool on hydrogen dewars or vents.
- Personnel should avoid wearing clothes made of nylon or other synthetics, silk, or wool. Pure cotton clothing is preferred. Nomex[™] (or the equivalent) material provides good antistatic qualities and provides some fire protection.
- Avoid electrostatic charge generation and accumulation. Lines, piping, and components within each system should be electrically bonded across each connection and grounded. Plastic and composite pipes and vessels should have surface resistivity of between 10⁵ and 10¹² Ω/m². Conductive coatings should be considered for use if necessary.
- Electrical circuit designs should consider types of electrical insulation used and bonding techniques to prevent arcing.

The energy required for ignition of flammable GH₂-air mixtures is so small that even spark-proof tools can cause ignitions. All tools should be used with caution to prevent slipping, glancing blows, or dropping, all of which can cause sparks. The use of non-sparking tools is recommended because they are less likely than standard tools to create a spark. All tools, including non-sparking tools, should be used with care. The use of non-sparking tools does not allow work to be done in an area where a potentially flammable atmosphere may exist.

Conductive and nonsparking floors are advised for areas where hydrogen gas can accumulate, such as during transfer operations or around in-process piping. Care should be exercised not to destroy the safety properties of the conductive floor by cutting grooves in it, painting it with nonconductive paint, or allowing it to get dirty.

4.3.5.5 Hot Objects, Flames, and Flame Arrestors

Flame producing devices shall be prohibited within the exclusion area around a hydrogen facility.

Operations causing heat, flames, or sparks, such as welding or cutting, shall not be performed with hydrogen present.

Internal combustion systems, motor vehicles, or equipment employing internal combustion engines shall be equipped with exhaust system spark arrestors and carburetor flame arrestors (hydrogen approved) when operated within the exclusionary zone with hydrogen present.

Only flame arrestors specifically designed for hydrogen applications shall be used. Flame arrestors designed for hydrocarbon flames will not stop hydrogen flames, and flame arrestors effective against hydrogen-air flames may not stop hydrogen-oxygen flames. Flame arrestors will quench a flame if they can remove sufficient heat from the gas. The small quenching distance of 0.06 cm (0.024 in.) for hydrogen makes it difficult to develop flame arrestors and explosion-proof equipment for hydrogen. Sintered metal flame arrestors for use with hydrogen are available from some welding equipment manufacturers. These are suitable for low flow, low pressure systems on the order of a few hundred standard cubic feet per hour and around 100 psi. They are usually available with an integral check-valve option. In the 1990s, petrochemical equipment manufacturers began developing arrestors for large process systems. Typical designs use finely corrugated metal ribbon wound into cylindrical elements. Designs vary depending upon the location of the arrestor in the piping system and the severity of the hazardous conditions expected (deflagration, detonation, continuous burning, etc.). Designs for more severe conditions typically have increased size, weight, and pressure drop. Most arrestors have few if any moving parts, but like filters, have small passages that could become plugged. Arrestors should be regularly inspected and maintained to ensure effectiveness.

4.3.6 Illumination

Adequate lighting shall be provided for night transfer operations (29 CFR 1910.103). All lighting components shall be consistent with the electrical classifications of the operation area.

4.3.7 Testing

Cryogenic components and systems shall be tested prior to acceptance for operational use. Piping and piping components shall be tested in accordance with ASME B31.3 and vessels in accordance with ASME BPVC. Testing shall include, but not be limited to, cold soak, thermal performance, pressure, leakage, welding quality, and vacuum retention.

4.4 Buildings and Test Chambers

Buildings and test chambers used in hydrogen service shall be consistent with the safety requirements of limiting personnel injury and facility damage in the event of hydrogen fire or explosion.

4.4.1 Buildings

Buildings or special rooms in which hydrogen (GH₂ and LH₂) is stored and used (nonpropellant) as allowed by 29 CFR 1910.103, NFPA 50A and 50B, shall be constructed in accordance with these standards. Some of the pertinent requirements are summarized in this section.

Buildings shall be constructed of light, noncombustible materials on a substantial frame. Window panes shall be shatterproof glass or plastic. Floors, walls, and ceilings should be designed and installed to limit the generation and accumulation of static electricity and shall have a fire resistance rating of at least two hours.

Explosion venting shall be provided in exterior walls or the roof only. The venting area shall not be less than 0.11 m²/m³ (0.033 ft²/ft³) of room volume (29 CFR 1910.103 1996). Vents may consist of one or a combination of the following, designed to relieve at a maximum internal pressure of 1.2 kPa (25 lb/ft²):

- Walls of light material
- Lightly fastened hatch covers
- · Lightly fastened, outward-opening swinging doors in exterior walls
- Lightly fastened walls or roof.

Doors shall be readily accessible to personnel. Doors should be hinged to swing outward in an explosion. Walls or partitions shall be continuous from floor to ceiling and securely anchored. At least one wall shall be an exterior wall, and the room shall not be open to other parts of the building.

Any heating in rooms and test cells containing hydrogen shall be limited to steam, hot water, or other indirect means.

4.4.2 Laboratory Setting, Test Chamber, Test Cell, Test Stand

Test facilities should be constructed to adhere to appropriate safety standards and guidelines as directed by the AHJ.

Test cells that cannot be ventilated sufficiently to cope with potential explosive hazards may eliminate this hazard by providing an inert atmosphere of nitrogen, carbon dioxide, helium, steam, or other inert gas. The test cell pressure should be higher than atmospheric to avoid inward leakage of air in such cases. The system design shall prevent any possibility of asphyxiation of personnel in adjacent areas. The system design shall provide for prevention of personnel entering the cell unless confined space entry procedures are strictly followed.

Oxidants may be reduced in a test chamber by using a partial vacuum. The vacuum should be sufficient to limit the pressure of an explosion to a value that the system can withstand. The chamber should withstand the blast pressure in this case. Heads, baffles, and other obstructions in a pipe run should be designed to consider reflected shock waves. Ultimate stress values may be used because the reaction time during an explosion is so short.

Laboratory settings are defined by small inventories of hydrogen (at the discretion of the AHJ) and bench top apparatus confined within ventilated cabinets or hood systems. Hydrogen accumulation is controlled with high ventilation rates (50 to 150 air changes per hour), detection systems and active controls that positively shut off the supply when an inadvertent release is detected or ventilation systems fail. The supply of hydrogen is subject to positive shut-off and limited to rates that preclude any dangerous buildup should component failure occur. The primary hazards are small fires and explosions. The same goals and strategies espoused elsewhere in this guide apply to measures developed for the laboratory scale.

4.4.3 Weather Shelter or Canopy

A weather shelter or canopy in an outdoor location shall be a structure enclosed by not more than two walls set at right angles and shall have vent space provided between the walls and vented roof or canopy. Such walls shall be constructed of noncombustible materials (29 CFR 1910.103).

4.4.4 Electrical Equipment

Electrical equipment shall conform to the requirements of NFPA 70 for Class 1, Group B locations. Materials for electrical equipment should be selected in accordance with established standards and guidelines as specified by the AHJ. Electrical terminals should not turn or loosen when subjected to service conditions. Terminal points should be protected from shorting by eliminating foreign objects and contaminants.

All electrical equipment for outdoor locations within 4.6 m (15 ft) of the system, separate buildings, and special rooms shall be in accordance with NFPA 70 (1993) for Class I, Division 2 locations for GH_2 systems (29 CFR 1910.103; NFPA 50A).

Electrical wiring and equipment located within 0.9 m (3 ft) of a point where connections are regularly made and disconnected, such as bayonet connections, shall be in accordance with NFPA 70 for Class 1, Group B, Division 1 locations for LH₂ systems. Electrical wiring and equipment located between 0.9 m (3 ft) and 7.6 m (25 ft) of a point where connections are regularly made and disconnected or within 7.6 m (25 ft) of a LH₂ storage container, shall be in accordance with NFPA 70 for Class I, Group B, Division 2.

When equipment approved for Class I, Group B, atmospheres is not commercially available, the equipment may be one of the following (29 CFR 1910.103):

- Purged or ventilated in accordance with NFPA 496
- Intrinsically safe
- Approved for Class I, Group C atmospheres

4.4.5 Ventilation

Any structure containing hydrogen system components shall be adequately ventilated when hydrogen is in the system. Ventilation shall be established before hydrogen enters the system involved and continued until the system is purged. Ventilation should not be shut off as a function of an emergency shutdown procedure. Suspended ceilings and inverted pockets shall be avoided or adequately ventilated. Annex B, Example 11 examines ventilation of occupied space in the presence of GH_2 releases.

Some ventilation requirements include the following:

- The normal air exchange should be about 0.3 m³ (1 ft³) of air per 1 m² (1 ft²) of solid floor in the space.
- Oxygen concentrations below 19.5% by volume require an air-line respirator in occupied spaces.
- Ventilation rates should be sufficient to dilute hydrogen leaks to 25% of the LFL; that is about 1% by volume for GH₂ (29 CFR 1910.106).

 A more stringent GH₂ concentration limit of 10% of the LFL or about 0.4% by volume is required for permit-required confined space (29 CFR 1910.146).

Adequate ventilation to the outdoors shall be provided. Inlet openings shall be located at floor level in exterior walls. Outlet openings shall be located at the high point of the room in exterior walls or roof. Inlet and outlet openings shall have a minimum total area of 0.003 m² (0.001 ft²) per 1 m³ (1 ft³) of room volume (29 CFR 1910.103).

Within the exclusion area, electric motors used to open vents, operate valves, operate fans, or power ventilators shall be in accordance with NFPA 70.

Hydrogen containers in buildings shall have their safety relief devices vented, without obstruction, to the outdoors at the minimum elevation to ensure area safety. Vents shall be located at least 15.2 m (50 ft) from air intakes (29 CFR 1910.103). The discharge from outlet openings shall be directed or conducted to a safe location.

 GH_2 systems of more than 85 standard m³ (3,000 standard ft³) shall not be located within 15.2 m (50 ft) of intakes for ventilation, air conditioning equipment, or air compressors (29 CFR 1910.134). Stricter limits apply for LH_2 or SLH_2 . The minimum distance to air compressor intakes, air conditioning inlets, or ventilating equipment shall be 23 m (75 ft) measured horizontally for all quantities.

4.5 Control Rooms

4.5.1 Structure

A pillbox, or concrete bunker, control room remote from a hydrogen test site is advisable. The control room of all hydrogen systems should provide a means of visual observation by direct or closed circuit television. A control room shall be designed to protect occupants from the most severe credible hazard.

A window opening into a test cell where excessive pressures or fragments could be present must be considered a hazard. A window should be made as small as practical and should be of bulletproof glass or the equivalent if one is necessary. A mirror system or a movable steel panel can be used in some cases.

A hydrogen-containing cell with an opening to another room should be maintained at a negative pressure relative to the communicating room if wall openings and such cannot be sealed.

4.5.2 Piping Systems

No hydrogen piping should enter the control room. Any hydraulic or pneumatic control valve should have a double diaphragm between the hydrogen line and the control room. Shutoff valves in hydraulic or pneumatic control lines entering a control room can be used for isolation of the control room for greater protection. Conduits should be sealed at the test cell end.

Existing GH₂ transmission lines buried underground in the control room area should be periodically proof tested and leak checked periodically. Buried lines are not allowed for new facilities.

4.5.3 Ventilation

Ventilation of a control room shall be in accordance with Section 4.4.5.

Particular attention should be paid to the ventilation or the air source for a control room that may, in an emergency, be enveloped in a combustible mixture or the products of combustion. Hydrogen detection equipment should be located within the control room if hydrogen could possibly be present.

4.5.4 Inert Gases

Ensure that instrumentation, gas sampling systems, and electrical conduits from purged electrical equipment cannot provide a leak path for inert gases to enter a control room.

4.6 Location and QD Guidelines

4.6.1 General

Location and QD requirements are based on the concept that the effects of fire, explosion, and detonation can be reduced to a tolerable level if the source of the hazard is kept far enough away from people and other facilities.

The location of hydrogen storage facilities should consider the effects of possible combustible cloud drift and the effects of thermal radiation if a fire occurs.

Hydrogen storage facilities shall be located so all personnel and facilities, whether involved in the operation or not, shall be adequately protected by appropriate design, including distance of separation, shielding, barricading, or other means. Consideration for the siting of hydrogen storage is first, to protect personnel and facilities as above; and second, to protect the hydrogen storage vessel and contents from external hazards, hazards associated with the storage and use of oxidizers, or other propellants and fuels.

Trailers, vehicles, or test articles that contain hydrogen should be located outdoors or in buildings specially constructed to avoid entrapment of hydrogen in the event of leaks or spills. Avoid areas of entrapment around the site if outdoors. Distance will have to be determined by the many variables that can affect the location. Some QD requirements for mobile storage units are given in DoD 6055.9.

4.6.2 Storage Type

Hydrogen storage is separated into two categories in this Guide — propellant and nonpropellant. These categories are generally defined by the application of the standards described below.

Storage for nonpropellant use at consumer sites shall be in accordance with the QD standards of 29 CFR 1910.103 (NFPA 50A and 50B).

Storage at sites where LH₂ is used as a liquid propellant shall be in accordance with the QD guidelines of DoD 6055.9.

The selection of which of the two QD standards given above should be applied to a hydrogen-storage installation must be determined for each individual installation. This selection will be determined by consideration of the applicability of each standard and by a hazard analysis. The hazard analysis should identify the primary hazard involved with the installation, such as: 1) hydrogen release and burning of a hydrogen/air mixture, and 2) explosion and fragment projectiles. The applicability and primary hazards covered by the two standards given above are addressed in sections D.4 and D.5 of Annex D.

4.6.3 Minimum Quantity Storage

QD determination should be handled on an individual basis by the AHJ for quantities of hydrogen less than the minimum specified in the standards or guidelines. Each situation should be evaluated based on the hazard presented by the specific quantity of hydrogen being considered.

4.6.4 Location and QD Standards for GH₂

The installation and location of GH_2 storage facilities shall conform to 29 CFR 1910.103 and NFPA 50A (1994).

The location of a GH₂ system, as determined by the maximum total contained volume of hydrogen, shall be in the order of preference indicated in Table A3.1 (29 CFR 1910.103).

The minimum distance from a hydrogen system of indicated capacity located outdoors, in separate buildings or in special rooms, to any specified outdoor exposure shall be in accordance with Table A3.2. Table A3.2 lists the exceptions to the stated distances for systems in which protective structures such as adequate firewalls are located between the GH₂ system and the exposure.

GH₂ systems of 84.9 m³ (3,000 ft³) or less located inside buildings shall be situated in the building so the following criteria are met:

- Adequately ventilated area as described in Section 4.4.5
- 6.1 m (20 ft) from stored flammable materials
- 7.6 m (25 ft) from open flames, electrical equipment, or other sources of ignition
- 15.2 m (50 ft) from ventilation intakes and air conditioning equipment
- 15.2 m (50 ft) from other flammable gas storage
- 7.6 m (25 ft) from concentrations of people
- More than one system of 84.9 m³ (3,000 ft³) or less may be installed in the same room, provided the systems are separated by at least 15.2 m (50 ft). Each system shall meet all the above requirements.

GH₂ systems of more than 84.9 m³ (3,000 ft³) shall not be located within 15.2 m (50 ft) of intakes for ventilation, air conditioning equipment, and air compressors (29 CFR 1910.134 1996).

4.6.5 Location and QD Standards for Nonpropellant Use of LH₂

LH₂ storage for nonpropellant use shall be in accordance with 29 CFR 1910.103 and NFPA 50B.

The location of LH₂ storage, as determined by the maximum total quantity of LH₂, shall be in the order of preference as shown in Table A3.3 (29 CFR 1910.103).

The minimum distance from LH₂ systems of indicated storage capacity located outdoors, in a separate building, or in a special room to any specified exposure shall be in accordance with Table A3.4 (29 CFR 1910.103 1996; NFPA 50B).

Portable LH₂ containers between 150 L (39.63 gal) and 189.2 L (50 gal) capacity housed inside buildings, not located in special rooms, and exposed to other occupancies, shall comply with the following minimum requirements:

- Located 6.1 m (20 ft) from flammable liquids and readily combustible materials
- Located 7.6 m (25 ft) from any electrical equipment not approved for use in a Class I, Division 2 area, and any other sources of ignition including process or analytical equipment
- Located 7.6 m (25 ft) from concentrations of people
- Located 15.2 m (50 ft) from air intakes, air conditioning equipment, or air compressor intakes
- Located 15.2 m (50 ft) from storage of other flammable gases or storage of oxidizing gases
- Welding, cutting operations, and smoking prohibited while LH₂ is in the room
- Area adequately ventilated as described in Section 4.4.5
- Safety relief devices on the LH₂ containers vented directly outdoors to a suitable vent stack or vented to a suitable hood

The minimum distance to air compressor intakes, air conditioning inlets, or ventilating equipment shall be 23 m (75 ft) measured horizontally for all quantities of LH₂.

4.6.6 Location and QD Guidelines for Propellant Use of LH₂

The storage of LH₂ for use as a liquid propellant shall be in accordance with DoD 6055.9 as applicable to an individual installation. The QD separation distance specified by DoD 6055.9 is based on factors such as the:

- Type of facility that is a potential explosion site (PES) and its construction (for example, degree of protection provided to limit blast and fragments).
- Ability of an exposed site (an inhabited building, for example) to resist possible explosion effects.
- Quantity of LH₂ involved.
- Quantity of any other chemicals, such as oxidizers and other fuels, involved.
- Possibility of LH₂ intermixing with other chemicals (for example, liquid oxygen).
- Compatibility of LH₂ with any other chemicals involved.
- Operations and conditions involved.
- Energetic reaction (for example, blast overpressure and container fragmentation) that could occur.

Additional information regarding DoD 6055.9 requirements is given in Section D.5 of Annex D.

4.6.7 Location and QD Guidelines for SLH₂

Specific experimental data for SLH₂ QD determinations are not available; therefore, no standards or guidelines are published for SLH₂ storage siting. The total mass of SLH₂ considered, SLH₂ can be treated as LH₂ equivalent and the appropriate QD standard or guidelines applied. However, the increased hazards associated with SLH₂, such as air contamination and pressure control, suggest that the QD guidelines for LH₂ propellant be used.

4.6.8 Location and QD Guidelines for Piping and Other Hydrogen Systems

There are no regulatory or consensus standards that provide QD guidelines for piping for the nonpropellant use of hydrogen. The QD guidelines provided by 29 CFR 1910.103, NFPA 50A and 50B apply to piping associated with a hydrogen storage vessel at a consumer location (see Section D.4 of Annex D), but do not apply to a consumer's piping for the nonpropellant use of hydrogen. The QD for hydrogen piping can be determined for a nonpropellant installation by a hazard analysis that identifies the hazards involved (such as thermal radiation, blast overpressure, and fragments) and then determines the appropriate separation distances required on the basis of these hazards and the exposures involved (such as personnel and buildings). The same hazard analysis technique may be used to determine the QD for consumer hydrogen systems that are not covered by regulatory or consensus standards.

DoD 6055.9 (see Section D.5 of Annex D) specifies that a minimum clear zone of 7.6 m (25 ft) to an inhabited building be maintained on each side of piping containing LH_2 that is used in a propulsion application.

4.7 Exclusion Areas

4.7.1 General

Standards and guidelines for the location of hydrogen systems effectively define an exclusion area in which access is limited to necessary personnel (must meet specified training requirements), equipment (must meet specified requirements for elimination or control of ignition sources), and operations (must be consistent with the requirements of safety to personnel and reducing risks to adjacent facilities) (29 CFR 1910.103; NFPA 50A and 50B). These standards and guidelines should be used as appropriate

for control of access and activities permitted in the vicinity of any hydrogen systems, such as storage, transmission piping, and test facilities.

The area within 4.6 m (15 ft) of GH_2 equipment, or 7.6 m (25 ft) of LH_2 equipment, shall be kept free of weeds, dry vegetation, and combustible materials (29 CFR 1910.103; NFPA 50A and 50B). Only combustible materials required for test purposes shall be allowed in the exclusion area.

QD standards and guidelines provide separation of hydrogen systems and inhabited areas and represent a minimum exclusion area.

Site specific requirements may establish an additional area, or control area, in which access is physically limited by fencing and control gates.

4.7.2 Access Control

Personnel access to any area containing hydrogen shall be considered as a potentially hazardous event and such entrance shall be by authorized personnel only. Personnel entering hydrogen system exclusion areas or control areas shall be provided necessary and sufficient clothing, equipment, detection devices, and respiratory devices as required (29 CFR 1910.132; 29 CFR 1910.133; 29 CFR 1910.134).

Requirements for access control to an area containing hydrogen include the following:

- Access shall be limited to authorized personnel (29 CFR 1910.103;NFPA 50A) for GH₂ systems.
- Access shall be limited to authorized personnel (29 CFR 1910.103;NFPA 50B) for LH₂ systems.
- The number of personnel at an operating location shall be the minimum consistent with safe and efficient operation for LH₂ systems. Tasks not necessary to the performance of a hazardous explosives operation shall not be performed in the same location as the hazardous operation. Personnel not needed for the hazardous operation will not be allowed in hazardous locations. Personnel limits shall allow for necessary supervision and transients. Sufficient personnel shall be available to perform a hazardous operation safely and, in the event of accident, to obtain help and aid the injured.
- Access is limited to authorized personnel for test chambers, test stands, and test cells. Such access shall be governed by guidelines established by the AHJ.
- Test cells and buildings in which combustible mixtures exist in the atmosphere shall not be entered under any condition. Personnel shall be warned of the presence of combustible mixtures or low oxygen concentrations (29 CFR 1910.1200). Warning systems such as approved vapor detectors, sensors, and continuous sampling devices shall be employed to ensure that the test cell environment is safe. The warning and detection devices shall operate audible and visible alarms. These systems shall be designed and installed to allow for the operation of equipment needed to reduce possible hazards. Examples include operation of auxiliary exhaust systems for venting upon the detection of flammable mixtures, operation of purging systems, and automatic operation of blocking and control valves.

4.7.3 Placarding, Posting, and Labeling

Exclusion areas and control areas shall have placards, postings, and labels displayed so personnel shall be aware of the potential hazard in the area.

The location of GH₂ systems shall be permanently placarded as follows:

HYDROGEN - FLAMMABLE GAS - NO SMOKING - NO OPEN FLAMES

Each portable container shall be legibly marked with the name "HYDROGEN." Each manifold hydrogen supply unit shall be legibly marked with the name "HYDROGEN" or a legend such as: "This unit contains hydrogen" (29 CFR 1910.103;NFPA 50A).

Storage sites for LH₂ systems shall be fenced and posted to prevent entrance by unauthorized personnel (29 CFR 1910.103; NFPA 50B). Signage shall include the following:

• Sites shall be placarded as follows:

LIQUEFIED HYDROGEN - FLAMMABLE GAS - NO SMOKING - NO OPEN FLAMES

Safety showers shall be placarded:

NOT TO BE USED FOR TREATMENT OF CRYOGENIC BURNS.

 A sign shall be placed on the container near the pressure-relief valve vent stack or on the vent stack that warns against spraying water on or in the vent opening.

Placards stating the maximum number of workers and transients permitted at any one time and the maximum amount of propellant materials and their Groups/Classes shall be posted for LH₂ propellant systems in a conspicuous place in all buildings, cubicles, cells, rooms, and storage areas containing propellant and similar materials. Personnel and material limits and the placard must be kept current and maintained for legibility. Placards must be of sufficient size and color that they are readily visible to personnel entering the work area. Local or DoD placards may be used.

Placarding, posting, and labeling for test chambers, test stands, and test cells shall be determined by the AHJ.

4.8 Protection of Hydrogen Systems and Surroundings

4.8.1 Barricades

All hydrogen-containing vessels, piping, and other equipment should be protected from potential sources of shrapnel. Barricades can provide necessary protection in many circumstances.

Barricades serve two purposes: to protect uncontrolled areas from the effects of a hydrogen system failure, and to protect the hydrogen system from the hazards of adjacent or nearby operations. It is highly desirable to design pressure vessels, piping, and components so failure caused by overpressure or material properties will not produce shrapnel; the system should leak its contents before it ruptures.

The possibility of system rupture caused by impact from adjacent hardware should be considered in locating the hydrogen system. Barricades should be located adjacent to the expected fragment source and in a direct line of sight between it and the facility to be protected because barricades have been shown to be most effective against fragments and only marginally effective in reducing overpressures at extended distances from them. If this is not possible, a barricade may be placed adjacent to the facility to be protected and in a direct line of sight between it and the expected fragment source.

Protection should be provided against failures that could yield shrapnel when reciprocating or high-speed equipment, such as a hydrogen pump, are required at hydrogen storage and use facilities. The equipment housing provides partial protection in many instances.

Appropriate fragment protection can be achieved in some applications by blast curtains and/or blast mats placed adjacent to the vessel or equipment to be protected.

The most common types of barricades are earthworks (mounds) and earthworks behind retaining walls (single-revetted barricades). A mound is an elevation of naturally sloped dirt with a crest at least 0.91 m (3 ft) wide. Single-revetted barricades are mounds modified by a retaining wall on the side facing the potential hazard source.

Barricades are constructed near potential explosion sources or in front of structures and facilities located near potential explosion sources. They are intended as protective devices to arrest fragments or attenuate blast waves. Results of analyses and tests show (Army AMCP-706-180; Baker et al. 1978) the following:

- Barricades reduce peak pressures and impulses behind the barricades; however, blast waves can reform under some circumstances.
- Single-revetted barricades are more efficient in reducing peak pressures and impulses than mounds.
- Values of peak pressure and impulse are greatly influenced by the height above ground and barricade location, dimensions, and configuration.
- Barricades are often needed in hydrogen test areas to shield personnel, dewars, and adjoining areas from blast waves and fragments. Barricades should be placed adjacent to the fragment source for maximum fragment protection (Army AMCP-706-180; Baker et al. 1978).
- Barricades, when required, should block the line-of-sight between any part of equipment from which
 fragments can originate and any part of the protected items. Protection of a public roadway shall
 assume a 3.66 m (12 ft) high vehicle on the road.

4.8.2 Liquid and Vapor Travel and Confinement

 LH_2 or SLH_2 spills, such as those that might occur from the rupture of a storage vessel, could result in a brief period of ground-level flammable cloud travel. The quick change from a liquid to a vapor and the thermal instability of the cloud cause the hydrogen vapors to mix quickly with air, disperse to nonflammable concentrations, warm up, and become positively buoyant. The presence of SLH_2 briefly prolongs this time period. Site specific information should determine whether natural dispersion of the spill or confinement of the spill is preferred.

Barricades should not cause excessive confinement that might lead to detonation rather than simple burning of escaped hydrogen. LH₂ spill tests conducted inside an open-ended (U-shaped) bunker without a roof produced detonation of the hydrogen-air mixture (Cloyd and Murphy 1965).

Although storage facilities for liquefied natural gas are required by law to include liquid-containment dikes, the use of dikes and barricades around LH₂ or SLH₂ storage facilities may prolong ground-level travel of the flammable cloud. It may be preferable to not use dikes and barricades to take advantage of the turbulent mixing of hydrogen with ambient air induced by vaporization of spills. Where it is necessary to locate LH₂ or SLH₂ containers on ground that is level with or lower than adjacent storage containers for flammable liquids or LOX, suitable protective means should be taken (such as diking, diversive curbs, sloped areas, and grading), with respect to the adjacent storage containers, to prevent accumulation of liquids within 15.2 m (50 ft) of the LH₂ or SLH₂ containers (NFPA 50B).

Pipeline ruptures may result in extended ground-level travel of a flammable cloud. Conditions also could be aggravated by the orientation of the pipeline for pipeline ruptures. Ground-level cloud travel may be prolonged by reduced spill or momentum-induced cloud turbulence and the long-term cooling of the ground for prolonged, gentle spills and pipeline ruptures. Hydrogen detectors should be positioned to indicate the possible ground-level travel of flammable mixtures.

No sewer drains shall be located in an area in which an LH₂ or SLH₂ spill could occur.

4.8.3 Shields and Impoundment Areas

The facility should include impoundment areas and shields for diverting spills to control the extent of liquid and vapor travel caused by spills. The loading areas and the terrain below transfer piping should be graded toward a sump or impoundment area. The surfaces within these areas should be cleared of flammable materials. Including barriers and insulated areas within the impoundment areas provides surface control of evaporation, especially during small leaks.

The use of crushed stone in the impoundment area can provide added surface area for LH₂ dissipation.

Ignition of hydrogen-air mixtures in free space usually results in combustion or deflagration, but with a confining, or partially confining, system geometry, a deflagration can evolve into a detonation. The facility

guidelines and planned installations should eliminate possible confining spaces developed by the equipment, tankage, and piping. With flame burning in and around a collection of pipes or structures, sufficient turbulence may develop to cause a deflagration to evolve to a detonation even in the absence of gross confinement.

4.9 Fire Protection

4.9.1 General

Preventive measures against fires should include automatic or manual process shutdown systems, sprinklers, deluge systems, water spray systems, dry-chemical extinguishing systems, and Halon systems. The fire safety policy shall be in accordance with the AHJ. Facilities shall provide appropriate automatic fire detection and suppression systems for hydrogen systems containing significant hazards.

Hydrogen fires normally are not extinguished until the supply of hydrogen is shut off because of the danger of reignition or explosion. Reignition may occur if a metal surface adjacent to the flame is not cooled with water or by other means.

Large quantities of water should be sprayed on adjacent equipment to cool the equipment and prevent its involvement in any fire that occurs. Combination fog and solid stream nozzles have been preferred to permit widest adaptability.

Care shall be exercised to prevent water from entering the vent openings when using water for hydrogen fire suppression involving LH₂ storage systems (NFPA 50B).

Small hydrogen fires have been extinguished by dry chemical extinguishers or with carbon dioxide, nitrogen, and steam.

Water spray systems shall be provided for hydrogen storage containers, grouped piping, and pumps where potential fire hazards exist. The system(s) shall be arranged to deliver a uniform spray pattern over 100% of the container surface, pumps, and adjacent piping. The minimum spray rate is 8.14 L/min·m² (0.2 gal/m·ft²) of exposed surface. Manual control stations shall be located outside the hazardous area, but within effective sight of the facility protected. Remote control capability shall be provided as directed by the AHJ. The design, installation, testing, and maintenance of fixed, water spray systems shall be in accordance with 29 CFR 1910.163 and NFPA 15. With the exception of preprimed, high-speed systems, water spray systems shall be of the deluge valve and open spray nozzle type. The systems are provided to protect defined hazardous equipment and areas and are not intended for complete facility protection.

The fire protection provided should be determined by an analysis of local conditions of hazard within the plant, exposure to other properties, water supplies, the probable effectiveness of plant fire brigades (such personnel must be trained to fight hydrogen fires), and the time of response and probable effectiveness of fire departments.

A fire hydrant or 2-in. (5.1-cm) diameter hose bib shall be provided adjacent to all LH₂ storage areas for wash down (NASA 1982).

4.9.2 Exposure Protection

Fires can damage objects by heat fluxes transmitted by radiation and convection. Much analytical and experimental work has been done on heat radiation from flames to surroundings. Existing models do not completely describe the complex phenomena. Factors that complicate the application of theory to heat radiation safety include changes in flame motion, turbulence, temperature profiles, flame size and shape, weather conditions, wind effects on back radiation, and flame emissivities.

Table A2.5 shows damage caused by various radiation levels. The damage also depends on the time history of the radiation. Atmospheric water vapor is very effective in absorbing the radiation because the water molecules are responsible for absorbing much of the infrared radiation (IR) from the hydrogen flame as shown in Figure A2.6. Figure A2.6 gives the mass of hydrogen needed to produce a 2 cal/cm² (0.051

Btu/in²) radiant flux as a function of distance from a hydrogen fire for various concentrations of atmospheric water vapor. As shown in Figure A2.6, a 1% concentration of water vapor in the atmosphere (corresponding to a relative humidity of about 43% at ambient temperature) will reduce the radiation flux at least two orders of magnitude at a distance of 100 m (328 ft) or greater.

Further comparisons of hydrogen fires with hydrocarbon fires show a lower smoke inhalation danger with hydrogen fires, but smoke inhalation remains a major cause of injuries and deaths in a hydrogen fire.

Figure A2.5 gives safe limits for the exposure of personnel and equipment to thermal-radiation-flux exposure levels that cover a wide range.

4.9.3 Deluge Systems

Strong consideration should be given to the installation of deluge systems along the top of storage areas for secondary fire protection. The deluge systems should be capable of being manually or automatically actuated. Also, any surface capable of becoming an ignition source should be cooled to not constitute a hazard. Fire extinguishing systems shall be used to protect manifold piping, relief vents, and transfer pump facilities but not for vent stack openings.

Rooms containing cryogenic and flammable fluids shall also be provided with fire and explosion protection. The rooms shall have a continuously operating exhaust system with a flow of about 0.3 m³/min·m² (1 ft³/min·ft²) of floor area. Upon detection of a flammable gas at 20% of the LFL, the exhaust capacity should be doubled.

Storage vessels shall be provided with water deluge systems designed to provide for at least 0.02 m³/min·m² (0.5 gal/min·ft²) on vessel surfaces and auxiliary fittings. Deluge systems shall be actuated by temperature rise detectors and remote, manual control. Enough hydrant outlets shall be located to enable use of charged hoses at each operation involving equipment in hydrogen service.

4.10 Documentation, Tagging, and Labeling of Storage Vessels, Piping, and Components

4.10.1 General

A uniform system for the identification of hydrogen vessels, piping, and components shall be established to promote greater safety and lessen the chances of error, confusion, or inaction, especially in times of emergency.

Each portable GH₂ container shall be legibly marked with the name "HYDROGEN" in accordance with 29 CFR 1910.103. Each manifold GH₂ supply unit shall be legibly marked with the name "HYDROGEN" or a legend such as "This unit contains hydrogen" (29 CFR 1910.103). Each LH₂ container shall be legibly marked (29 CFR 1910.103):

LIQUEFIED HYDROGEN - FLAMMABLE GAS

A sign shall be placed on the container near the pressure-relief valve vent stack or on the vent stack that warns against spraying water on, or in, the vent opening (NFPA 50B).

4.10.2 Documentation

Each hydrogen pressure vessel or pressurized system (including vacuum systems) shall be marked to indicate it is certified or recertified for use and any special constraints or instructions required for safe operation of the pressure vessel or pressurized system (including vacuum systems).

Documentation for each pressure vessel or pressurized system shall be prepared and revised or updated periodically. Documentation shall identify the organization or individual responsible for the pressure vessel or pressurized system and contain, as a minimum, a pressure vessel or pressurized system description, list of available drawings and documentation, analysis results, certification requirements, unique in-service

inspection requirements, and results of the most recent inspection. See Section 4.1.2 for additional information.

4.10.3 Tagging

The storage vessels, piping, and components, shall be tagged and coded to indicate the following as appropriate:

- Contents
- Capacity
- Direction of flow as appropriate
- Maximum allowable working pressure (MAWP)
- Hydrostatic test pressure
- · Certified test pressure
- Date, month, and year of last hydrostatic test
- Manufacturer part number
- Operating temperature
- Component number or identification per appropriate process schematic

4.10.4 Labeling

The labeling of piping and components shall be uniform and convey the necessary information (ASME A13.1) including the following:

- The lettered legend will be marked "HYDROGEN (by form)" in black letters on a yellow field.
- The label will be white lettering on a blue field for piping and components for purge gases; or white lettering on a green field for purge liquids; however, labels with black letters on a yellow field should be used for high-pressure or high-temperature purge fluids.
- Labels with white letters on a red field should be used for piping and components for fire quenching materials.
- Arrows shall be used to indicate direction of flow.
- Additional information shall be included as necessary.
- Legends shall be applied close to valves or flanges and adjacent to changes in direction, branches, where pipes pass through walls or floors, and at intervals sufficient for identification on straight pipe runs.
- Attention shall be given to viability of the legend. Where pipe lines are located above or below the normal line of vision, the lettering shall be placed below or above the horizontal centerline of the pipe.

4.11 Instrumentation and Monitoring

4.11.1 Instrumentation

A hydrogen system should be adequately instrumented for the following:

- Monitor and control its operation.
- Provide performance data.

- Provide warnings and/or alarms for out-of-limits conditions.
- Indicate a hazardous condition, preferably with sufficient notice to permit it to be addressed.
- Instrumentation used in a hydrogen system shall meet Class I, Division I or II, Group B requirements of NFPA 70 as appropriate.

Instrumentation used in a hydrogen system should:

- Be compatible with hydrogen and with all operating conditions such as temperature and pressure;
- Permit local and/or remote operation and monitoring of the hydrogen system;
- Have the appropriate range, accuracy, and response time.

Instrumentation used in a hydrogen system that provides safety information should be redundant in number and type of transducer (pressure indicated locally by a pressure gage and remotely by a pressure sensor). Data from the instrumentation should be displayed so the operator has a clear indication of the status of the hydrogen system.

Computer control and data acquisition systems should be used whenever possible and carefully checked to verify they are properly interfaced with the instrumentation transducers. The instrumentation system (computer, data acquisition, transducer, and wiring) should be calibrated at installation in a hydrogen system and should be periodically recalibrated as directed by the AHJ.

Ancillary instrumentation, such as sampling equipment and a mass spectrometer for purity analysis, should be available on an as-needed basis.

Instrumentation used in LH₂ and SLH₂ systems should be selected and installed to minimize heat leaks to the cryogenic fluids. A wide selection of instrumentation options are available for the parameters commonly monitored in a hydrogen system.

4.11.2 Hydrogen Detection

Hydrogen gas is colorless, odorless, and normally not detectable by human senses. Means shall be provided for detecting the presence of hydrogen in all areas in which leaks, spills, or hazardous accumulations may occur. Refer to Section 6 for requirements and specifications for hydrogen detection.

A combination of portable and fixed installation hydrogen sensors should be used. Portable hydrogen detectors should be available for personnel entering an area in which hydrogen is leaking or may have leaked.

Hydrogen detectors shall meet Class I, Division I or II, Group B requirements of NFPA 70 as appropriate.

4.11.3 Fire Detection

A hydrogen flame is nearly invisible, and the emissivity of a hydrogen fire is low; consequently, means should be provided for detecting the presence of a hydrogen flame in all areas in which leaks, spills, or hazardous accumulations of hydrogen may occur.

A hydrogen fire will cause changes in the surroundings that can be used to detect the fire. The changes are commonly called the signature of the fire. Although the nonluminous hydrogen flame makes visual detection difficult, there is a strong heat effect and turbulence of the surrounding atmosphere.

The hydrogen fire detection system should be capable of monitoring a large area over considerable distances. The effects of lightning and sunlight should be considered in the use of infrared (IR) detectors.

The combination of portable and fixed installation hydrogen fire detectors should be used. Portable hydrogen fire detectors should be available for personnel (including the fire department) entering an area in which a hydrogen fire is possible.

Fire detectors shall meet Class I, Division I or II, Group B requirements of NFPA 70 as appropriate.

4.11.4 System Monitoring

Remote television monitoring of a hydrogen system should be considered if the system is not visible from the control center.

4.12 Examination, Inspection, and Recertification

4.12.1 General

All storage and piping installations, including their components, shall be inspected before the initial operations to ensure compliance with the material, fabrication, workmanship, assembly, and test requirements. The completion of all required examinations and testing shall be verified. Verification shall include, but should not be limited to, certifications and records pertaining to materials, components, heat treatment, examination and testing, and qualification of welding operators and procedures.

Comprehensive control is essential for all systems used in GH₂, LH₂, and SLH₂ installations. It is highly recommended that a quality control program be established that will satisfy the AHJ's requirements and engineering design for all vessels, piping, components materials, and test equipment.

Material identification is required for all piping and components used in fabrications and assemblies subjected to LH₂ temperatures. No substitutions for the materials and components specified in the engineering design are permitted except when the substitution has written approval of the AHJ.

4.12.2 Examinations

Examinations shall be performed in accordance with the ASME BPVC. Visual examinations should verify dimensions, joint preparation (4.12.1 specified to be maintained under positive gas pressure should be examined to ensure conformance to the requirements.

4.12.3 Testing and Recertification

All pressure vessels and systems shall be designed, inspected, tested, operated, and maintained in accordance with the requirements and standards specified by the AHJ.

After installation, all piping, tubing, and fittings shall be tested and proved hydrogen gas tight at operating pressure and temperature using the appropriate test or tests (29 CFR 1910.103; NFPA 50A and 50B) as follows:

- The hydrostatic test pressure should be 1.5 times the MAWP.
- Pneumatic tests shall be approved by the AHJ. The pneumatic test may be used in lieu of the
 hydrostatic test for hydrogen systems designed or supported so they cannot safely be filled with liquid
 or if the vessel or system cannot be readily dried, or is to be used in services in which traces of the
 testing liquid cannot be tolerated. The substitution requires that the parts of the system, when
 possible, are previously tested by hydrostatic pressure. The pneumatic test pressure should be
 1.25 times the MAWP.
- After a cryogenic system is constructed and has passed the hydrostatic or pneumatic test, the system shall be cold tested with LN₂. Storage vessels that cannot support the weight of a 100% load of LN₂ should be filled with the equivalent weight of LN₂ that corresponds with a 100% load of LH₂ or SLH₂. LN₂ temperature should be maintained in the new system for a minimum of one hour.

All welds shall be tested as required by ASME BPVC and ASME B31.3. Unless the inner LH_2 or SLH_2 container is fully radiographed, all welds in or on the shell and heads, inside and outside, should be tested by the magnetic particle method, the fluorescent dye penetrant method, or by the ultrasonic testing method as appropriate. All cracks and other defects found should be repaired in accordance with the proper repair procedures.

A system to be used in hydrogen service shall be leak tested prior to operation. Leak testing generally occurs in conjunction with the pressure testing of the system. The system should be leak tested to the extent possible with inert gases before LH₂ is introduced into the system. Personnel and equipment shall be adequately protected during a leak check involving hydrogen, whether GH₂, LH₂, or SLH₂. Leak testing methods that may be used will be specified by the AHJ.

4.12.4 Records

Records shall be made and retained for each pressure vessel and pressurized system (including vacuum) inspection and recertification examination. The records shall be retained for the life of the pressure vessel or pressurized system as directed by the AHJ. The records should include the following:

- Date of inspection or recertification examination
- Identification of system, component, and piping
- Test method (for example, hydrostatic, pneumatic, or sensitive leak test)
- Test fluid
- Test pressure
- Hold time at maximum test pressure, if over 10 min
- Test temperature
- Locations, types, and causes of failures and leaks in components and welded joints, types of repair, and other applicable test records
- Approval by safety or design engineer specified by the AHJ

4.12.5 Schedule

The inspection and recertification schedule for each pressure vessel and pressurized system (including vacuum) shall be established by the pressure system manager as appointed by the AHJ. The AHJ shall provide guidelines for the creation of inspection and recertification schedules.

5 Hydrogen Storage Vessels, Piping, and Components

5.1 General Requirements

5.1.1 General

All vessels, piping, fittings, vent stacks, and other system components used in hydrogen service shall be designed and operated to provide maximum protection to personnel and equipment.

All pressure vessels, pressurized components and pressurized systems (including vacuum) shall be designed, fabricated, installed, operated, periodically inspected, maintained, repaired, and certified/recertified in accordance with the applicable codes, standards, and guidelines as specified by the AHJ.

5.1.2 Special Considerations

The application of standards such as the ASME BPVC, ASME B31.1, and ASME B31.3 for hydrogen storage and piping require special considerations as a consequence of the unique properties of hydrogen, such as hydrogen embrittlement.

5.1.3 GH₂ Temperature Considerations

The reference to GH_2 in this Guide normally has implied ambient temperature. However, the designer should identify the hydrogen systems in which GH_2 is at cryogenic temperature and select materials and design equipment appropriate to those conditions. This distinction is characterized in 29 CFR 1910.103 by using ASME B31.1 for GH_2 above 244 K (-20 °F), and ANSI B31.3 for cryogenic GH_2 below 244 K (-20 °F).

5.2 Storage Vessels

5.2.1 Fixed and Mobile Storage Systems for GH₂.

Containers for GH₂ storage shall be designed, constructed, and tested in accordance with appropriate requirements of ASME BPVC or designed, constructed, tested and maintained in accordance with DOT specifications and regulations as appropriate. Permanently installed containers shall be provided with substantial noncombustible supports or firm noncombustible foundations (29 CFR 1910.103; NFPA 50A).

Large volumes of GH_2 should be stored outdoors in mobile or fixed cylinders. Mobile tube trailers of approximately 2,000 m³ (70,000 ft³) capacity, pressurized to about 16.5 MPa gage (2,400 psig), have been state of the art for many years and have not exhibited any undue operating problems. GH_2 vessels for service to 68.9 MPa (10,000 psia) are available. Vessels for very large volumes and higher gas pressures have not always been trouble free. Guidelines include the following:

- Materials shall be selected in accordance with ASME BPVC and 49 CFR.
- No unrelieved penetrations of the sidewalls shall be made. Enter through the forged heads if a
 pressure gage is needed.
- Provisions shall be made for visual inspection of the interior in accordance with 49 CFR for mobile storage units.

Gas tube trailers carrying more than one gas shall be prohibited unless logistical considerations absolutely mandate their use. Connecting fittings shall be keyed, sized, or otherwise configured so that it is physically impossible to cross-connect incompatible systems without malicious intent to do so (49 CFR). GH₂ tube trailers shall be equipped with safety shutoff valves that are normally closed and require continuous power to open and remain open. The valves will automatically return to fully closed upon the removal of the power. This is in addition to manually operated main shutoff valves. The valve cabinets shall be well ventilated.

An example of the importance of keeping separate manifolds for hydrogen and oxygen is a mishap that involved an explosion in a tube of a tube trailer that contained a mixture of hydrogen and oxygen. The accident occurred after a hydrogen tube trailer and an oxygen tube trailer were simultaneously connected to the same manifold. Insufficient barriers and incorrect purging procedures led to the damage of one shutoff valve and subsequent flow of higher pressure oxygen into one tube of the hydrogen trailer. Ignition was probably caused by contamination traveling through a valve at high velocity.

Common gas facilities for fuels and oxidants are not recommended. Such facilities require the approval of the AHJ.

Fixed storage vessels shall be located in accordance with the approved QD tables in 29 CFR 1910.103 (see Section 4.6 of this Guide).

5.2.2 Fixed and Mobile Storage Systems for LH₂

Containers for LH₂ storage, whether for nonpropellant or propellant use, shall be designed, constructed, and tested in accordance with appropriate requirements of the ASME BPVC or applicable provisions of API 620. Portable containers for LH₂ shall be designed, constructed, and tested in accordance with DOT specifications and regulations. Permanently installed containers shall be provided with substantial noncombustible supports securely anchored on firm noncombustible foundations. Steel supports in excess of 18 in. (46 cm) high shall be protected with a coating having a two hour fire resistance rating (29 CFR 1910.103; NFPA 50B).

LH₂ vessels should be designed to include thermal protection systems to minimize the evaporation losses. Common types of insulation systems employed are the following:

- A vacuum equal to that required under operating conditions
- High vacuum plus powders such as perlite, silica aerogel, diatomaceous earth, fused alumina, and phenolic spheres
- Multiple layers of highly reflecting radiation shields separated by spacers or insulators plus a high vacuum
- Materials with low thermal conductivity (Hastelloy™ (or the equivalent), titanium) used to support the insulation

The inner vessel should be designed to have a vapor-tight seal in the outer jacket or covering to prevent air condensation and oxygen enrichment within the insulation. Condensed air in the insulation systems may explosively expand as it reverts to a gas when the LH₂ is emptied from the tanks or pipes.

Construction materials for surfaces exposed to a cryogen should retain the necessary mechanical properties and not tend toward low-temperature embrittlement (see Section 3).

Fixed storage vessels for nonpropellant or propellant use shall be located in accordance with the appropriate QD requirements in Section 4.6.

Pressure relief is required for the inner vessel and vacuum jacket (see Section 5.5). Annex B, Example 4 examines pressure rise in storage vessels. Bottom openings on LH₂ containers should be avoided where possible (preventing an uncontrollable leak path if a valve or connector should fail).

Safety techniques and devices include such special provisions as elimination of static electricity buildup, locking devices to prevent loosening of parts, flexible grounding straps from the compartment doors to the main vessel frame structure, and the protection of all fittings, valves, gauging devices, manifolding, etc., against damage caused by collision or overturning.

Recommended procedures, driver training, and basic operations shall be consistent with 29 CFR and 49 CFR (see Section 8).

All LH₂ vessels, stationary and mobile, should be equipped with remote control shut off valves, but manually operated valves may be used under the following conditions:

- The loading operations and valve are attended by two trained operators using the buddy system if approved by the AHJ
- The pressure of the vessel does not exceed the MAWP

A mobile vessel used as a component of a test facility should have a remote-operating, fail-safe shut off valve. A manual override should be provided for use if the power fails.

5.2.3 Fixed and Mobile Storage Systems for SLH₂

5.2.3.1 **General**

The design principles given above for LH₂ are directly applicable to the handling of SLH₂; however, the properties of SLH₂ call for additional considerations such as those described below.

5.2.3.2 Cryogenic Considerations

The use of SLH_2 requires greater care than when operating with NBP LH_2 . The operating temperature of SLH_2 is lower than that for NBP LH_2 , 13.80 K (-434.8 °F) versus 20.27 K (-423.2 °F). The vapor pressure of SLH_2 at its operating temperature is 7.04 kPa (1.02 psia); therefore, the container should be designed for operation at subatmospheric pressure. The heat of fusion (melting of the solid) for SLH_2 is 58.29 J/g (25.1 Btu/lb) compared with 445.6 J/g (191.7 Btu/lb) for vaporization of NBP LH_2 .

It is necessary that systems for SLH₂ ground storage and transfer be built with the lowest possible heat input (highest quality thermal insulation). Also provisions should be made for transferring the liquid-solid mixture to preclude any accumulation of solid particles that could block or plug valve seats, instrumentation ports, or relief valve openings.

The tolerable amount of heat leak into SLH₂ storage dewars depends on actual sizes and logistics. Current technology for the construction of large-scale cryogenic storage dewars indicates that maintaining SLH₂ at a 50% mass fraction of solid would require a replenishment rate of SLH₂, 50% solid by mass, of 0.5% per day. Without replenishment, the solid fraction would decrease by about 0.5% per day.

5.2.3.3 Storage and Upgrading

A replenishment or upgrading process is needed to eliminate the possibility of a decrease in solid fraction and/or to upgrade the SLH₂ above the level at which it was originally transferred into the storage dewar. This can be accomplished by placing a filter at the outlet of the storage vessel leading to a return transfer line, that, with the fill line from the SLH₂ production unit, will allow for the continuous transfer of SLH₂ to the storage dewar with the triple-point liquid being returned to the slush generator. With proper attention to maintaining the ullage pressure, this technique can be used for replenishing or upgrading the SLH₂ in a flight vessel.

A provision for stirring the SLH_2 in ground or flight storage vessels may be required to prevent the solid particles from settling or agglomerating. The stirring will also tend to destroy the thermal gradients that will require helium pressurization of the vessel to avoid subatmospheric pressures. The stirring may also be necessary to maintain a free passageway through the solids that tend to accumulate at the filter entrance.

5.2.3.4 Materials Selection

From a structural standpoint, the proper selection of materials to be used can be assured by using only materials shown to be suitable for LH₂ service (see Section 3). The desirability of maintaining thermal gradients and the thermal conductivity of appropriate structural materials should be considered along with the strength-to-weight ratios, thermal expansion coefficients, and low-temperature ductilities.

Although the temperature differences between LH₂ and SLH₂ should not cause any problems when using materials suitable for LH₂ service, the possibility remains that the solid particles flowing in SLH₂ could, over time, cause the softer materials to erode in certain places such as in a valve seat.

5.2.3.5 Subatmospheric Pressure Considerations

Although efforts are made to avoid storing and handling the SLH_2 at subatmospheric pressures, the possibility of pressure collapse is always present. Negative pressures will occur if the evaporative-cooling production method is used. Additional safety precautions should be taken to preclude contamination and enhance the operational safety of the system.

Systems for handling SLH₂ should be designed to make the maximum use of welded construction a primary requirement. Demountable joints should be used only where absolutely necessary.

State-of-the-art leak detection techniques are to be used in fabricating all of the equipment in which SLH_2 is to be handled. A leak detection test should be performed after thermal cycling from ambient temperature down to at least 77 K (-320 °F) (LN_2 temperature).

SLH₂ handling equipment shall be continuously monitored for the intrusion of air from the atmosphere after placing the equipment into service. Samples of SLH₂ taken from the stored fluid are warmed to room temperature and subjected to gas analysis (mass spectrometry or gas chromatography). This technique has the disadvantage of having to determine how closely a given sample represents the contents of the entire stored volume (Edeskuty and Stewart 1996).

Instrumentation tubes, flanges, wire pass-throughs, and valve stem packings compromise, to some extent, the integrity of the otherwise more robust and impenetrable, all-welded construction of a SLH₂ system. Entries into the system such as these provide potential leak points where atmospheric air could enter the system, especially when it is below atmospheric pressure.

The SLH₂ system design should maximize the use of external volumes, known as guard volumes, under a high vacuum or pressurized with helium, surrounding the portions of the system at (or potentially at) subatmospheric pressure. The pressure in the guard volume shall be monitored and provided with an alarm to warn of the loss of vacuum or helium in the guard volume. Vacuum pump systems and discharge points of pressure-relief valves and rupture disks deserve special attention for prevention of leakage into the system.

5.2.3.6 Fluid Quantity Measurements

It is not difficult to determine the total volume of SLH₂ by using liquid level measurements; however, this procedure does not determine the mass. The level of the solid fraction can be measured when settling is allowed to take place in the SLH₂ system. Without a greater knowledge of the degree of packing of the solid, the total mass of the stored SLH₂ will still be unknown. Nuclear radiation attenuation or other means whereby the mass concentration of a representative sample can be measured should be considered and the results assumed to be valid for the entire contents of the vessel.

5.2.3.7 Thermal Acoustic Oscillations

Thermal acoustic oscillations and their propagation are a periodic source of elevated pressure and can pump large quantities of energy into the main storage volume. Designing SLH₂ systems with favorable aspect ratios and surge volumes is a promising method for reducing this problem.

5.2.3.8 Instrumentation

The distribution of solid particles within the liquid is very difficult to determine, and it changes during production, storage, aging, stirring, and transfer. At present, the contents of a containment vessel need to be observed to determine production, storage, aging, and other critical characteristics of the SLH₂.

A number of designs for visual observation ports have been reported and generally are composed of two or three quartz, glass, or sapphire windows separated by a high-vacuum as thermal insulation.

5.2.3.9 Transportation

At present, the difficulties in handling and maintaining SLH₂ mixtures make it unlikely that SLH₂ would be produced at a remote location and transported to the use site. Thus, transporting SLH₂ for significant distances is not considered, and a discussion of mobile storage systems for SLH₂ is not presented.

5.2.4 Aerospace Pressure Vessels

The AHJ shall specify standards applicable for aerospace pressure vessels. Pressure vessels for use in flight or ground support equipment may be designed to Mil-Std-1522 or equivalent. Standards providing criteria for using fracture control techniques to design, fabricate, test and operate aerospace pressure vessels are commonly used.

When technically possible, each pressure vessel should be designed to accommodate proof and verification tests. Tests should be performed to confirm the design, manufacturing processes, and service life. Qualification tests should be conducted on flight-quality hardware. All aerospace pressure vessels should be subjected to an acceptance test.

5.2.5 Supports

The design of vessel support members should account for all concurrently acting loads transmitted into such supports. These loads, in addition to weight effects, should include loads introduced by service pressure and temperature, vibration, wind, earthquake, shock, and conditions such as thermal expansion and contraction.

The design and construction of supports for inner vessel systems should be optimized with respect to structural and thermal operational requirements.

5.3 Piping Systems

5.3.1 General

The design of a piping system for hydrogen use shall consider the pressure, temperature, and various forces applicable to the design of a hydrogen piping system. Special consideration shall be given for the unique properties of hydrogen, such as hydrogen embrittlement. Piping systems for hydrogen use shall be designed based on the most severe condition of coincident pressure, temperature, and loading. The most severe condition shall be the one that results in the greatest required pipe thickness and highest flange rating. Piping as used in this guideline includes pipe, tubing, flanges, bolting, gaskets, valves, relief devices, fittings, and the pressure containing portions of other piping components. It also includes hangers and supports and other equipment items necessary to prevent overstressing pressure containing components.

Piping systems include all hydrogen transmission lines and associated components including the lines and fittings connecting test articles to hydrogen supplies. Safety reviews of piping systems designs shall be in accordance with those detailed in Sections 4.1 and 4.2.

Piping materials and designs should be in accordance with ASME B31.3. However, ASME B31.3 generally does not specify materials to be used in hydrogen piping systems, but provides guidance and limitations on the selection of some materials acceptable for use in piping systems. This code provides some useful properties, such as minimum temperature and maximum allowable stress values as a function of operating temperature for these materials (Table A5.3). GH₂ systems should also conform to the special requirements of NFPA 50A and LH₂ systems to NFPA 50B.

Section 3 discusses general materials recommended for use in hydrogen piping and system components. See "Standard for Hydrogen Piping Systems at Consumer Locations" (CGA G-5.4) for additional information on hydrogen piping systems.

Piping and pressure containing components shall be proof tested (ASME B31.3). Additional testing may be included as required, such as pneumatic flow testing at operating conditions and cold testing.

Facility and transfer piping systems shall include safeguards in accordance with ASME B31.3 for protection from accidental damage and for the protection of people and property against harmful consequences of vessel, piping, and equipment failures. Barriers should be considered for operator protection particularly from metal parts associated with pump failures. Within a process area, hydrogen transport piping shall be treated similar to hydrogen storage in that all such piping shall be isolated by an exclusion zone in which access is restricted and certain types of operations are prohibited while hydrogen is present in the piping system (see Section 4.6.8).

New piping for GH₂ or LH₂ shall not be buried. Piping shall be placed in open trenches with removable grating if placed below ground. Existing, buried GH₂ piping shall be operated in accordance with the conditions of retroactivity detailed in Section 1.1.7.

All piping shall be periodically tested as part of the recertification of the pressure system (Section 4.12). The piping and components shall be tagged and coded as described in Section 4.10.

Hydrogen lines should not be located beneath electric power transmission lines. Electric wiring systems permitted above hydrogen lines should comply with the appropriate code (NFPA 50B).

The metal components of a hydrogen system shall be electrically bonded in accordance with NFPA 70. This includes tanks, regulators, valves, pipes, vents, vaporizers, and receivers (mobile or stationary). Sufficient grounding connections should be provided to prevent any measurable static charge from accumulating on any component. Each flange should have bonding straps in addition to metal fasteners, which are primarily structural.

Joints in piping and tubing should be made by welding or brazing. Mechanical joints such as flanges should only be used for ease of installation, maintenance, and other similar considerations.

Provisions shall be made for the expansion and contraction of piping connected to a pressure vessel to limit forces and moments transmitted to the pressure vessel, by providing substantial anchorage at suitable points, so there shall be no undue strain to the pressure vessel.

5.3.2 Supports

The design of piping support members should account for all concurrently acting loads transmitted into such supports. These loads, in addition to weight effects, should include loads introduced by conditions such as service pressure and temperature, vibration, wind, earthquake, shock, and thermal expansion and contraction.

All supports and restraints should be fabricated from materials suitable for the service conditions. Any attachments welded to the piping should be of material compatible with the piping and service conditions. The stress for the base material of all parts of supporting and restraint assemblies should not exceed the allowable stress at the operating temperature for the part in question.

Pipe supports for thin-wall vacuum-jacketed pipe should be located at points on the jacket with doubler plates or load-spreading saddles.

The design and construction of supports for inner piping systems should be optimized with respect to structural and thermal operational requirements.

5.3.3 Piping for GH₂

Materials for GH₂ piping systems and components must be suitable for the stress, temperature, pressure, and exposure conditions.

Conditions considered to characterize hydrogen embrittlement failures include temperature, pressure, and hydrogen purity. Failures of piping and components are most severe at room temperature, at high pressure, and with very pure hydrogen. (The problems are reduced at cryogenic temperatures.)

High-pressure gas manifolds are to be constructed of suitable materials (Section 3) and of welded construction wherever possible. Expansion or contraction should be accommodated, and adequate supports should be provided.

5.3.4 Piping for LH₂ and SLH₂

Most LH_2 or SLH_2 lines are vacuum jacketed or insulated to reduce heat input and prevent the condensation of atmospheric air. The piping vacuum jacket systems should be separate from the vacuum systems of the main hydrogen storage and handling systems. The jacket design should consider the thermal flexibility of the inner line and allow the jacket to follow its natural thermal displacement. The vacuum jacket shall have its own separate pressure-relief system. Annex B, Example 5 examines the effect of insulation for LH_2 lines on the heat leak rate.

Bellows expansion joints usually are placed in the outer jacket when they are used. Expansion joints have been used in the inner line, but their placement may affect the thermal stress forces transmitted to the outer jacket and add potential vacuum leak sources. Bellows should not be extended or compressed at installation to make up for deficiencies in length or for proper alignment. The inner pipe usually is supported within the vacuum jacket by spacers in the annulus. The spacer design and location should take into account the thermal loading during cool down and forces transmitted to the jacket. The spacers should also support the dead weight of the inner line under all imposed conditions. Piping systems must have sufficient flexibility to prevent thermal expansion or contraction causing piping failures or leaks. Expansion loops or InvarTM (or the equivalent) piping are alternatives to expansion joints.

An LH₂ or SLH₂ system built of stainless steel has a thermal contraction of about 0.3% from ambient temperature to 20 K (-423 °F). Long runs of piping require a support at intervals to allow for axial motion with lateral and vertical motion restrained.

Expansion joints used in vacuum jacket systems normally have the lowest pressure rating in the vacuum system and should be marked to indicate pressure rating and direction of flow. Swivel joints and connections that allow for three degrees of freedom should be installed in piping exposed to differential movements, such as ship-to-dock piping.

Piping systems must have sufficient flexibility to prevent excessive stresses caused by thermal expansion, contraction, or movements of piping supports and terminals. Consideration should be given to the following:

- Failure of piping, supports, or anchors from overstress or fatigue
- Leakage at joints
- Detrimental stresses or distortion in piping or in connected equipment resulting from excessive thrusts and moments in the piping
- Resonance with imposed or flow-induced vibrations
- Cryogenic bowing in horizontal pipe lines because of the stratified flow of a single liquid layer on the
 bottom of the pipe. Consideration shall be given to the large forces normally generated by bowing in
 designing pipe guides and main and intermediate anchors for bellows expansion joints. Cryogenic
 pipelines should be operated in regimes in which stratified flow does not occur.

Each section of cryogenic piping in which liquid lockup is possible shall be equipped with protective devices to control overpressures, particularly those caused by insulation failures and fires. Annex B, Example 3 examines pressure rise caused by liquid lockup in a line.

Insulation for LH₂ or SLH₂ piping shall have a self-extinguishing fire rating. Other fluid lines should also be protected from freezing because of proximity to the LH₂ or SLH₂ lines; a thermostatically controlled heater should be considered to provide protection. Cryogenic piping systems should not be painted white. Frost is the best indicator of insulation failure.

Low points (traps) on liquid discharge piping are to be avoided to prevent the accumulation of contaminants and trapping of liquid. Low-point drains should be provided if traps are unavoidable.

Any uninsulated piping and equipment operating at LH₂ or SLH₂ temperatures shall be installed away from (and not above) asphalt or other combustible surfaces and protection provided for incompatible metals subject to cold embrittlement.

SLH₂ transfer lines should be designed to eliminate possible flow segregation and settling or filtering of the solid hydrogen particles.

Piping and piping components shall be designed for at least the MAWP of the hydrogen supply or the pump output pressure, which is the MAWP, when such systems are supplied by a pump.

5.3.5 Bending and Forming Piping

Pipe may be bent to any radius that will result in arc surfaces free of cracks and substantially free of buckles. Flattening of a bend, as measured by the difference between the maximum and minimum diameters at any cross section, should not exceed 8% of the nominal outside diameter for internal pressure and 3% for external pressure.

Piping components may be formed by any suitable hot or cold working method (swaging, lapping, or upsetting of pipe ends, extrusion of necks, etc.), provided such processes result in formed surfaces that are uniform and free of cracks or other defects.

The various piping components should be assembled, in a shop or as a field erection, so the completely erected piping conforms with the specified requirements of the engineering design.

Any compound or lubricant used in threaded joints shall be suitable for the service conditions and shall not react unfavorably with hydrogen or the piping materials. Threaded joints to be seal welded shall be made up without any thread compound.

5.3.6 Double Block and Bleed

Consideration should be given to using a double-block-and-bleed arrangement to isolate supplies from other parts of the system when designing hydrogen systems (Edeskuty and Stewart 1996). A double-block-and-bleed arrangement as shown in Figure 1 below, is a positive way to ensure that hydrogen leaking through a shutoff valve does not enter other parts of a system where it is not desired. In normal flow operation, the two line valves are open and the vent valve to the atmosphere is closed. The shutdown and safe position is for the two line valves to be closed and the vent valve open. With the valves in these positions any leakage from the line valves will be vented to the atmosphere rather than flowing into another part of the system. A disadvantage of the double-block-and-bleed arrangement that must be considered is that when the main flow line is cold and the vent valve is open to the atmosphere the potential exists for condensation and freezing of air and moisture inside the cold piping.

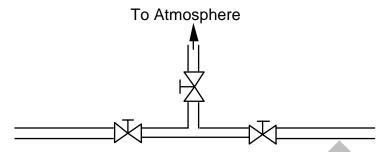


Figure 1 — Double-block-and-bleed arrangement

5.4 Components

5.4.1 Joints in Piping and Tubing

5.4.1.1 General

Joints in piping and tubing may be made for GH_2 by welding or brazing or using flanged, threaded, socket, or compression fittings. Joints in piping and tubing for LH_2 or SLH_2 preferably shall be made by welding or brazing; flanged, threaded, socket, or suitable compression fittings may be used. Brazing materials shall have a melting point above 811 K (1,000 °F) (NFPA 50A and 50B).

The fused joint is recommended in GH₂, LH₂, or SLH₂ systems because of its simplicity and high reliability. Hard soldering and welding often can meet the bonding requirements, but the welded joint takes preference for safety (29 CFR 1910.103). This is a potential safety factor because a melted joint could release additional large quantities of fuel in the event of an accidental fire. Such failures could develop into a chain reaction in large systems. All general purpose GH₂, LH₂, or SLH₂ systems should be constructed of high melting point materials for this reason.

5.4.1.2 Welded Joints

Welding is the first preference for all hydrogen systems, and all forms of welding can be used (ASME B31.3). The type of weld to be used generally is determined by factors other than the fact that the system is for hydrogen use. Gas tungsten arc (HeliarcTM or the equivalent) welding generally is preferred for joining light-gage stainless steel and often is preferred for construction of vacuum-jacketed equipment. Conventional arc techniques also are used extensively, especially for heavy-gage material for which cost is a strong factor. Filler material and stress-relieving requirements are determined by the parent material to be joined, and normal standard practices should be followed.

To identify individual welds, mark with crayon or paint not conducive to corrosion of the base metal, unless another method is specified by the engineering design. No markings shall be allowed on the inner pipe of vacuum-jacketed joints to preclude out-gassing. Welds, including additions of weld metal for alignment, shall be made in accordance with a qualified procedure and by qualified welders or welding operators.

The AHJ is responsible for the welding done by personnel within his jurisdiction, and shall conduct the required tests to qualify the welding procedures and the welders or welding operators. Contractors are responsible for welding done by their personnel. The contractor having jurisdiction must also approve and accept a performance qualification made by a welder or welding operator for another employer. If approval is given, acceptance is limited to performance qualification on piping using the same or equivalent procedure wherein the essential variables are within the limits set forth in ASME BPVC Section IX and ASME B31.3.

5.4.1.3 Threaded Joints

Threaded joints with a suitable thread seal are acceptable for use in GH₂ systems but are to be avoided in LH₂ or SLH₂ systems. Consideration should be given to back-welding threaded joints for GH₂ systems inside buildings. Bayonet joints should be used for LH₂ or SLH₂ transfer operations.

5.4.1.4 Mitered Joints

Mitered joints may be used in LH₂ or SLH₂ piping systems under the following conditions:

- A joint stress analysis has been performed and the appropriate safety committee has approved.
- The number of full-pressure or thermal cycles will not exceed 7,000 during the expected lifetime of the pipe system.
- Full-penetration welds should be used in joining miter segments.

5.4.1.5 Quick-Connecting Flange Joints

Quick-connecting flange joints are recommended for connecting loading arms from ships to storage, to ensure minimum times for making or breaking connections, increasing safety in an emergency. Docking and unloading facilities should be designed for possible impact loads, protection from LH₂ or SLH₂ spills, and rapid deberthing of ships. Pier loading facilities shall be located at least 300 m (1,000 ft) from bridges. Effort should be maintained to keep the ship-to-shore recirculation loops cold so heat leakage is reduced, geysering is minimized, and problems related to warm vapor returning to the tanks are eliminated.

5.4.1.6 Silver Braze Joints

No unique problems have been encountered with silver braze materials. The choice of braze composition is determined by ease of application to the material to be joined; however, cadmium containing silver brazes shall not be used (29 CFR 1910.1027). Silver brazes are recommended for joining copper-base materials and dissimilar metals such as copper and stainless steel. The melting point must be greater than 811 K (1,000 °F) (NFPA 50A and 50B).

5.4.1.7 Soft Solder Joints

Soft solder joints are not permissible in hydrogen systems. Soft solder has a low melting point and will quickly fail in fire, potentially releasing more hydrogen. Also, soft solders containing tin may become crumbly and lose all strength at cryogenic temperatures (CFR 29 1910.103). Soft solder may be used as appropriate in nonhydrogen portions of the system such as a vacuum jacket.

5.4.1.8 Bimetallic Transition Joints

Bimetallic transition joints should only be used as necessary. Emphasis of the design should be to reduce stress on the joint.

5.4.2 Pipe Connections

A pipe having a branch connection is weakened by the opening made in it, and it requires reinforcing unless the pipe wall is sufficiently thicker than required to sustain the pressure. Greater flexibility should be provided in the smaller line, of designs of small branches out of large and heavy runs, to accommodate thermal expansion and other movements of the larger line. Branch connections should be made in piping systems as follows:

- Fittings (tees, laterals, and crosses) should be made in accordance with standard procedures.
- Outlet fittings should be welded.
- The branch pipe may be welded directly to the run pipe with or without reinforcement.

Extruded outlets in the run pipe, at the attachment of the branch pipe, should be butt-welded.

5.4.3 Fittings

Tube fittings of flared, flareless, or compression type may be used for tube sizes not exceeding 5.1 cm (2 in.) outside diameter within the limitations of applicable standards. The designer shall determine that the type and the material of the fitting selected is adequate and safe for the design conditions in the absence of standards, specifications, or allowable stress values for the material used to manufacture the fitting (ASME B31.3).

5.4.4 Flanges

Flanges should be designed and manufactured in accordance with the ASME BPVC. Blanks to be used for test purposes only should be designed in accordance with the ASME BPVC, except the design pressure should be at least equal to the test pressure and the allowable stress should be as great as 90% of the specified minimum yield strength of the blank material. Flanges using a soft gasket should use a raised-face flange with a concentrically serrated face.

5.4.5 Flexible Hoses

Flexible hoses pressurized to greater than 1.14 MPa (165 psia) should be restrained at intervals not to exceed 1.83 m (6 ft) and should have an approved restraint device such as the Kellems hose containment grips attached across each union or hose splice and at each end of the hose. The restraint devices should be secured to an object of adequate strength to restrain the hose if it breaks.

Hose containment methods and devices that differ from standard devices should be approved by the AHJ. Hose containment methods and devices are described in NASA center documents such as the Kennedy Handbook (1983).

Flexible hoses carrying LH₂ or SLH₂ should be vacuum jacketed. The inner flexible hose should be the load-carrying member.

5.4.6 Expansion Joints

Bellows expansion joints used in hydrogen piping systems may be convoluted or toroidal and may or may not be reinforced. Lap-welded tubing should not be used.

A fatigue life able to withstand the full thermal motion cycles should be a design requirement, but the life of the bellows should not be less than 1,000 full thermal movement and pressure cycles in any case (ASME B31.3).

Expansion joints should be marked to show the direction of flow. Unless otherwise stated in the design specifications, flow liners should be provided when flow velocities exceed the following values:

- Expansion joint diameter less than or equal to 15.2 cm (6 in.): gas flow velocity of 48 m/s per m of tube diameter (4 ft/s per in. of tube diameter) or liquid flow velocity of 24 m/s per m of tube diameter (2 ft/s per in. of tube diameter)
- Expansion joint diameter greater than 15.2 cm (6 in.): gas flow velocity of 300 m/s per m of tube diameter (25 ft/s per in. of tube diameter) or liquid flow velocity of 120 m/s per m of tube diameter (10 ft/s per in. of tube diameter)

The hydrostatic end force caused by pressure, as well as the bellows spring force and the guide friction force shall be resisted by a rigid external anchor or a tie rod configuration in all piping systems containing bellows.

An expansion joint should be installed in a location that is accessible for scheduled inspection.

Pressure tests of piping systems should be performed with the bellows expansion joints installed in the line with no additional restraints so the expansion joint cross connections or external main anchors carry the full pressure load. Tests should not be performed until all anchors and guides are securely in place.

The quality of the expansion joint can be ensured by any, or all, of the following tests, as specified by the systems engineer. As a minimum, tests 1) and 2) should be performed.

- 1) 100% dye penetrant inspection of the outside surface of the bellows tube weld before forming
- 2) 100% x-ray inspection of the bellows tube weld before forming
- 3) 100% dye penetrant inspection of the outside surface of the bellows tube weld after corrugating
- 4) 100% percent dye penetrant inspection of all pressure-retaining attachment welds
- 5) Soap-bubble leak test (air under water or helium mass spectrometer)
- 6) Hydrostatic testing at 1.5 times design pressure

The stability of the bellows element in the expansion joint shall be demonstrated by conducting a standard manufacturer's hydrostatic test of 1.5 times design pressure on at least the first item of each design.

When a large pressure gradient exists in a line such as a flare stack line or a vertical line and the pressure gradient is largely because of elevation (as with storage tanks, etc.), the bellows load may be additionally restrained or the bellows may be blocked off or removed. Another system test should be conducted at 1.5 times the bellows operating pressure to demonstrate adequacy of the anchors.

Multiple expansion joints and bellows should not be used in cryogenic service.

5.4.7 V-Band Couplings

Properly applied V-band couplings are approved for connecting vacuum-jacketed LH₂ or SLH₂ lines. Suppliers offer a wide selection of couplings that range from light to heavy duty and cover a number of flange angles and thicknesses. Visual inspection often is not adequate to distinguish between some of the similar types. It is mandatory to use part numbers to ensure proper application of the couplings.

Male and female flanges should mate properly before applicable V-band couplings are applied. The couplings are not expected to correct any misalignment inherent in fabrication or make a leak-free joint where flanges or O-rings have been damaged.

Extreme care should be exercised in applying and tightening the couplings to ensure a leak-free joint.

Vacuum-jacketed piping must not be subjected to excessive tension forces. Flexible sections often are employed; however, to be effective, the sections should be connected with sufficient slack (or compression) when warm so they will not be excessively stretched as the system is cooled to the operating temperature.

5.4.8 Valves

Valves subjected to cold hydrogen flows shall be suitable for cryogenic service.

A shut off valve shall be located in the liquid product withdrawal line as close to the container as practical. On a container of over 7.6 m³ (2,000 gal) capacity, the shutoff valve shall be a remote control type with no connections, flanges, or other appurtenances (other than a welded manual shutoff valve) allowed in the piping between the shutoff valve and its connection to the inner container (29 CFR 1910.103).

Vessels used as components of a test facility should have remote operating fail-safe shutoff valves. A manual override must be provided for use if the power fails.

Excess flow valves for GH₂ service are self-actuated devices that shut off flow when the built-in sensing mechanism detects that a preset maximum flow rate has been reached. The excess flow valve may be used to provide immediate hydrogen shut off in the event of failure of the piping system or equipment.

Rupture disks or relief valves must be installed in all enclosures that contain liquid or can trap liquids or cold vapors for protection against the hazards associated with ruptures. Rupture disks or relief valves may not be necessary if the liquid or the cold vapor trapped between two valves can be relieved through one of the valves at a pressure less than the design operating pressure.

5.4.9 Transfer Connections

5.4.9.1 General

Connections must be keyed, sized, or located so they cannot be cross-connected to minimize the possibility of connecting incompatible gaseous fluids or pressure levels. The connections and fittings to be disconnected during operations should be provided with tethered end plates, caps, plugs, or covers to protect the system from contamination or damage when not in use. Pressure relief shall also be provided if cold fluid can remain trapped in the lines.

5.4.9.2 GH₂ Transfer Connections

GH₂ connections from over-the-road tube trailers or supply systems should conform to the specific safety design and material requirements. The cylinder pressure should not be allowed to fall below 172 kPa (25 psig) gage to prevent the infiltration of air into the gas cylinders.

Piping, tubing, and fittings must be suitable for hydrogen service at the pressures and temperatures involved. The joints in piping and tubing preferably should be made by welding. Provisions must be made for expansion and contraction.

Flexure installations to be used at high pressures must be designed so restraint is provided on the hose and adjacent structure. The restraints must be provided at 1.83 m (6 ft) intervals and at each end to prevent whiplash in the event of a rupture.

5.4.9.3 LH₂ and SLH₂ Transfer Connections

Vessels should be connected to rigidly mounted test facility piping with supported and anchored flexible metal hose insulated for low-temperature services at the desired pressure. Recommendations for flexible hoses include a maximum allowable slack of about 5% of the total length. The hose restraints should be at least 50% stronger than the calculated impact force on an open line moving through the flexure distance of the restraint for greater safety. Sharp bends and twists should be avoided in the routing of flexible hose. A minimum of 5 times the outside diameter of the hose is considered acceptable as a bend radius.

Each end of the LH₂ discharge hose should be equipped with male bayonet couplings capable of connecting to its mating female connector as approved by the AHJ. The fasteners for the couplings may be bolted flange, spanner nut, or V-band fasteners designed for the required operating pressure.

Quick-connecting flange joints are recommended for connecting loading arms, especially from ships to storage. Being able to make or break connections quickly provides greater safety in an emergency.

The mobile supply should be located to provide safe access, but the flange to flange distance of the flexible hose should not be greater than 3 m (10 ft) (CGA V-6). The pressure range of the transfer equipment must be rated equal to or greater than the tanker design pressure.

If condensation or frost appears on the external surface of a hose during use, the hose should be taken out of service until the vacuum (insulation) has been restored.

5.4.10 Gaskets and O-Rings

5.4.10.1 General

The selection of a gasket for obtaining a leak proof joint depends on the mechanical features of the assembly, system operating conditions, fluid characteristics, and gasket material characteristics and design. The general characteristics are interdependent, and a change of one condition can alter the choice of gasket.

Even with proper assembly, design, and sound installation, subtle changes because of fatigue, temperature changes, and vibration may reduce gasket material resilience and cause a leak. Torque loss becomes a serious consideration and requires a gasket material that will be minimally affected by thermal gradients.

The contact surface finish of the assembly face and the type of assembly affect gasket selection. The bolting should be adequate to produce the degree of gasket flow required for a pressure-tight seal. A relatively rough surface finish requires heavier bolting to achieve the requisite gasket flow than a smooth surface finish. Concentrically serrated faces are preferred.

Flanges should be leak checked periodically. Flanges with soft gaskets in LH₂ and SLH₂ systems should be retorqued periodically.

5.4.10.2 Metal O-rings

Metal O-rings have proven satisfactory for sealing flanges on LH₂ piping and vessels only when coated with a soft material and used on smooth surfaces.

Type 321 stainless steel O-rings with a coating such as Teflon™ (or the equivalent) or silver should be used in stainless flanges with stainless bolts. Likewise, Teflon™ (or the equivalent)-coated aluminum O-rings should be used in aluminum flanges with aluminum bolting. Using similar materials avoids the leakage possibility from unequal contraction or corrosion of dissimilar metals.

Surface finishes in the O-ring groove and contact area should be in accordance with the manufacturer's specifications. All machine or grind marks should be concentric.

5.4.10.3 Gaskets, Seals, and Valve Seats

PCTFE (polytrifluorochloroethylene) or TeflonTM (or the equivalent) (polytetrafluoroethylene) can be used in LH₂ or SLH₂ systems for the following sealing applications:

- Valve seats may be PCTFE or modified Teflon[™] (or the equivalent) (Fluorogreen[™] (or the equivalent) is preferred).
- Gland packing or seal only if it is maintained near ambient temperatures as in an extended bonnet of a shutoff valve. The contraction or shrinkage of Teflon™ (or the equivalent) when cooled from ambient to cryogenic temperatures allows leakage.
- Flat, thin gaskets for tongue-and-groove flanges, where the gasket is shrouded on four sides. Virgin
 Teflon™ (or the equivalent) gaskets should be captured on all sides to prevent cold flow and
 subsequent leakage.

Correct installation of a gasket is of major importance if subsequent leaks are to be averted. Flange faces should be cleaned and as closely aligned as possible. The gasket should be centered. The bolts should be tightened by hand then two bolts, 180° apart, should be tightened. The operation should be repeated until all bolts are uniformly torqued. The amount of torque applied at each step during tightening should be small at the start to avoid cocking the flange faces. It may be necessary in LH₂ or SLH₂ applications to retighten bolts to compensate for thermal forces. Means to prevent bolts from loosening should be provided.

A raised-face flange is recommended for high pressures or low temperatures. Metallic gaskets have been used successfully with raised-face flanges for pressures to 20.6 MPa (3,000 psig). A tongue-and-groove flange is desirable for most gasket materials for higher pressures. A confining flange is mandatory if a plastic such as TeflonTM (or the equivalent) is used. Twenty-five percent glass-filled TeflonTM (FluorogreenTM or FluorogoldTM or the equivalent) should be used for flanges that are not seal welded.

Care should be taken to accommodate the cold flow characteristics of the material for raised-faced, separated flanges using 25% glass-filled Teflon[™] (or the equivalent) or other, similar soft gaskets. Retorque flanges a minimum of 30 h after initial torque, after each cryogenic use until torque relaxation has ceased, and on an annual basis.

5.5 Overpressure Protection of Storage Vessels and Piping Systems

5.5.1 General

Safety devices shall be installed on tanks, lines, and component systems to prevent damage by overpressure. The required relieving capacity of any pressure-relief device shall include consideration of all the vessel and piping systems it protects (29 CFR 1910.103; CGA S-1.1; CGA S-1.2; CGA S-1.3). Annex E contains additional information on pressure-relief devices.

5.5.2 Safety Valves

Safety valves should be designed so the movable parts cannot stick or seize even with unequal heating or cooling. Packings that might hinder the working of the safety valve through friction should not be used.

The design of a safety valve installation requires careful attention to be paid to all loads acting on the system. All components in a safety valve installation should be given consideration, including the complete piping system, connection to the main header, safety valve, valve and pipe flanges, downstream discharge or vent piping, and system support.

The relief or safety valves shall be set to limit the maximum pressure to not exceed the MAWP as specified in Annex E.

Safety and relief valves should be direct spring or deadweight loaded. Pilot valve control or other indirect operation of safety valves is allowed if the design is such that the main unloading valve automatically opens at the set pressure or less and is capable of discharge at its full rate capacity if the pilot or auxiliary device should fail.

Relief valves shall be sized to accommodate the maximum flow capacity of the pressure source.

All materials used in the construction of overpressure protection systems, including the pressure-relief devices, should be suitable for the operating temperature of the tankage and piping systems. Pressure-relief devices and the inlet and discharge piping should be designed and installed to minimize moisture accumulation and ice buildup from atmospheric condensation that could cause them to fail to function properly. The pressure-relief devices preferably should be located to relieve vapor-gas rather than liquid.

The openings through all pipe fittings between a piping and tankage system and its pressure-relief device should have at least the area of the device inlet. The flow characteristics of the upstream system should be such that the pressure drop will not reduce the relief capacity below that required or adversely affect the proper operation of the pressure-relief device. The pressure drop should not exceed 5% of the set pressure.

Pressure-relief devices discharge vents should not be connected to a common line when feasible. The effect of the back pressure that may develop when valves operate should be considered when discharge lines are long or outlets of two or more valves having different relief set pressures are connected to a common line. Discharges directly to the atmosphere should not impinge on other piping or equipment and should be directed away from platforms and other areas used by personnel because the discharge gas

may ignite and burn. Reactions on the piping system because of actuation of pressure-relief devices should be considered, and adequate strength should be provided to withstand the reactions.

Stop valves should not be installed between the tankage and piping being protected and their protective devices, or between the protective devices and the point of discharge without approval of the AHJ. Stop valves may be installed in other areas under specific conditions. An authorized person should continuously observe the operating pressure and should have an arrangement for relieving the system in the event of overpressure if stop valves are to be closed while the equipment is in operation. Also, stop valves may be used in pressure-relief piping if they are constructed or positively controlled so closing the maximum possible number of stop valves will not lower the capacity of the unaffected pressure-relief devices below that required.

A rupture disk or relief valve shall be installed in every section of a line where liquid or cold gas can be trapped. This condition exists most often between two valves in series. A rupture disk or relief valve may not be required if at least one of the valves will, by its design, relieve safely at a pressure less than the design pressure of the liquid line. This procedure is most appropriate in situations where rupturing of the disk could create a serious hazard.

The installation design shall include a study of the discharge piping and pipe supports. Reactive force can be imposed on the valve or outlet piping and transmitted to the valve inlet and associated piping. This force could cause extensive damage if the discharge piping is unsupported. Also to be evaluated are the effects of sudden chill down stresses and thermal contractions that may result from the opening of a protective device. Annex B, Example 7 is an example of the analysis of a pressure-relief valve.

5.5.3 Rupture Disks

Rupture disks are designed to break at a specific pressure, temperature, and tensile strength of the disk; therefore, the pressure at which a disk will rupture is directly affected by the temperature. The disks should be located to limit temperature variations. Rupture disks are susceptible to failure from cyclic loading. Rupture disks have finite lifetimes and routine replacement should be planned.

It is recommended that because of fatigue or creep, the stamped bursting pressure of rupture disks be sufficiently above the intended operating pressure to prevent premature failure of the rupture disks when they are used. Rupture disks may be used in tandem or series with relief or safety valves and may be located upstream or downstream of the valves, provided the system design allows it. Rupture disks should be kept properly aligned.

Only materials suitable for the working conditions are to be used for rupture disks. Rupture disks should be rated as specified in Annex E.

The response pressures of rupture disks at room temperature should be determined when testing, in addition to checking their dimensions. Rupture disks should be provided with a protective device to catch broken fragments of the bursting element and should be arranged to be protected against damage from outside.

The rupture disks may be installed upstream of the relief valve if the disk rupture pressure is less than the MAWP, methods of detecting disk failure or leakage are present, sizing is correct, and there is no chance for the disk failure to interfere with the operation of the relief valve.

Under approved conditions, rupture disks may be installed downstream of relief valves to prevent mixing of the atmosphere and the escaping hydrogen in the event of a temporary low-flow overpressure condition or to prevent ice from building up in the relief device. The rupture pressure under such conditions should not exceed 20% of the set pressure of the relief device and the space between the relief valve and the disk should be vented to a system in which back pressure will not adversely affect the operation of the relief valve.

A rupture disk may be installed in parallel with a second type of relief device of which the relief valve usually is set to relieve before the rupture disk.

Weather protection of the vent opening from the relief devices should be included.

5.5.4 Supplemental Pressure Relief

Supplemental pressure-relief devices should be installed to protect against excessive pressures created by exposure to fire or other unexpected sources of external heat. Relief devices installed in any section of the vessel and piping systems limit the allowable working pressure. The special secondary relief valves, set at 110% of the MAWP, should be provided wherever it is possible to trap liquid in an appreciable fraction of the line volume. The supplemental relief device should be capable of limiting the pressure to 121% of the MAWP.

Transient pressure surges associated with chill-down flow instabilities, water hammer, and cavitation should be considered in designing and installing supplemental relief systems.

5.5.5 Failure Modes

Failure modes that must be considered in the design and operation of protective pressure-relief systems include the following:

- Pressure buildup associated with the phase change or temperature rise caused by the normal heat leak into the section. The minimum capacity of the primary protective device should be determined by the heat leak rate. The device should be located as near as possible to the highest point in the line section (Annex B, Example 3).
- The overpressure potential associated with connection to a high-pressure source of any type pump, pressure-relief valve, or direct connection through a flow-limiting orifice requires the existence of a pressure switch to cut off the source of high pressure but does not eliminate the need for the primary protective device. The primary protective device should be located as close as possible to the high-pressure source. The primary relief device should be designed and sized to accommodate liquid flow if it is possible to vent LH₂ through it. Additionally, consideration should be given to protection from overpressure caused by abnormal conditions peculiar to LH₂ tankage and piping, such as insulation failures.
- Each section of a vacuum jacket system should be protected with a relief device. This device, possibly a rupture disk, should limit the pressure in the annulus to not more than 10% above the lesser of the external design pressure of the inner line or the design pressure of the jacket. Capacity consideration for the jacket should be based on a catastrophic failure.

5.6 Hydrogen Vent and Flare Systems

5.6.1 General

Hydrogen shall be disposed of by venting unused, unburned hydrogen and/or by using suitable burning systems. Hydrogen systems and components must be equipped with venting systems satisfactory for normal operating requirements and for protection in the event of an emergency. All dewars, storage, and flow systems shall be equipped with unobstructed vent systems designed to safely dispose of hydrogen and prevent the entry and accumulation of atmospheric precipitation. The vent systems should be equipped for weather protection, and any lines leading to the vent stack should be long enough to warm the hydrogen to above liquid-air temperature. Over-the-road dewar vent systems should be connected to a building hydrogen vent system when the dewar is parked near a building. The vent systems should be designed to carry vented hydrogen to safe-release locations above the roof. The vent systems should be designed to support the excess load caused by venting the liquid or gas. The vent stacks shall be placed

^{††} Per paragraph UG-125[©] (2) Section VIII, Division 1 of the ASME BPVC

to avoid possible contamination of air intakes leading into nearby buildings and designed to keep air out of the stack.

5.6.2 Venting

The allowable quantities of hydrogen that may be vented are subject to conditions such as wind direction, wind velocity, proximity of inhabited buildings, vent stack height, local discharge limitations, or other environmental restrictions. Quantities of hydrogen of 0.113 to 0.226 kg/s (0.25 to 0.50 lb/s) have been successfully vented from a single vent 5 m (16 ft) high. Multiple roof vents at least 5 m (16 ft) apart across the prevailing wind may be used. The use of multiple vents is preferred rather than using a collection header and a single vent stack for multiple sources requiring venting.

Interconnecting vent discharges to the same vent stack may over-pressurize parts of the vent system. The vent system must be designed to handle the flows from all discharges, or the flow may back into parts of the system. The vent system should be designed and sized so as to prevent excessive chattering of any check valves in the system (this will help prevent any potential sparks, or loose particles, from metal-on-metal striking). Inadequate designs also may effectively change the release pressure on all relief valves and rupture disks connected to the vent system. Overpressure in the vent system, which may be very high (NFPA 68), can cause overpressure and failure of connected apparatus. Design guidelines for hydrogen vent systems for GH₂ and LH₂ installations at consumer sites and recommendations for their safe operation are provided in CGA G-5.5, "Hydrogen Vent Systems."

High-pressure, high-capacity vent discharges and low-pressure vent discharges should not be connected to the same vent stack unless the vent capacity is sufficient to avoid overpressurizing the weakest part of the system. The discharge from vacuum pumps should be ducted to suitable vents.

Small quantities of hydrogen may be disposed of outdoors through vent stacks of suitable heights. A molecular seal, flapper, check valve, or other suitable device should be provided in the flow and transfer systems near the atmospheric discharge to limit the backflow of air. The vent piping should be purged to ensure that a flammable mixture will not develop in the piping when hydrogen is introduced. Nitrogen gas may be used as a purge and blanketing gas when process temperatures are above 77 K (-320 °F); for lower temperatures, helium gas must be used. Hydrogen gas may be ignited (by static electrical charges for example) as it leaves the vent piping. A helium or nitrogen gas purge, as appropriate, should be made available to extinguish any flame, and the vent stack must be located to prevent a fire hazard if adequate atmospheric dispersion is not available. Gas or liquid backed into vessels or transfer lines by emergency shutdown conditions must be released or vented in a safe manner.

5.6.3 Hydrogen Disposal by Burning

Large quantities of hydrogen that cannot be safely handled by roof vent or stack systems are best disposed of in a burn-off system in which the liquid or the gas is piped to a remote area and burned with air in a multiple burner arrangement. Such systems shall have pilot ignition, warning systems in case of flameout, and means for purging the vent line. The design of a hydrogen disposal system also must provide sufficient assurances of the following:

- Hydrogen issuing from the flare stack will be disposed of safely
- The flare stack system will prevent explosions within the stack
- The radiation flux levels from burning hydrogen will not harm personnel or damage the facility.

Diffusion flames are most frequently used in flare stack operations. Combustion air comes from the open atmosphere around the downstream end of the stack and ideally mixes with hydrogen outside the stack. The stack may have single or multiple outlets. A pilot flame external to the stack is usually used to ignite the flare and help maintain combustion. The pilot often uses a hydrocarbon fuel such as propane or natural gas to provide a more visible flame for monitoring purposes. Temperature sensors or other detectors may be used to verify that the stack remains lit (see Section 6.2).

Hydrogen flow through the flare stack must be within the operational velocity that provides for stable combustion. The low density of hydrogen compared with air can create back-streaming and partial mixing within the stack under certain conditions, leading to instability, flashback, or blow-off behavior similar to that observed in premixed flames.

Under low velocity conditions, the buoyancy of hydrogen can create a negative pressure region within the vent pipe into which the heavier surrounding air can migrate, creating a flammable mixture within the stack and causing the flame to drop or flash back into the stack. In multiple discharge stacks, air can be drawn back through one or more ports, creating a flammable mixture inside the manifold. Experiments performed with hydrogen and helium in a single discharge stack demonstrated that high concentrations of air (60 to 85% by volume) could occur at substantial distances within the flare stack during the upward flow of the vented gases (Grumer 1970). Figure A4.1 gives experimental data showing when the flame was observed to enter the flare stack as a function of stack diameter and hydrogen flow. Discharge velocities should be from 10% to 20% of the sonic velocity in hydrogen to prevent air from entering. This will result in a flow rate well above the curve in Figure A4.1. When the hydrogen flow is too low to maintain this velocity, a continuous purge or a slight positive pressure shall be provided, or the stack shall be designed to limit back flow of air into the exit piping (see Section 5.6.2).

While higher flow at the vent discharge can prevent migration of air back into the vent, negative pressures can be created and maintained inside the vent system where high velocities may occur. Extra care must be taken to ensure the vent system is leak tight to avoid air intrusion and possible detonation.

High exit velocity flow can also lift the flame away from the flare discharge or blow it out entirely, releasing unburned hydrogen into the atmosphere. The concept of boundary velocity gradient used in evaluating the stability of premixed flames has been applied to diffusion flames as well. Figure A4.2 shows a plot of boundary velocity gradient versus percentage of hydrogen in hydrogen/inert gas mixtures defining the blowout and stable flame regions. Note that the blowout boundary velocity gradient for pure hydrogen will typically require supersonic flow unless the diameter of the stack is extremely small. However, the addition of an inert gas (for stack purging, for example) will lower the blowout velocity gradient limit. In situations where a large percentage of the flow is inert gas, a discharge velocity of 10 to 20% of the sonic velocity of pure hydrogen may be too high.

Figure A4.3 shows predicted flame shapes in crosswinds for hydrogen, methane, and benzene. Annex B, Example 8 analyzes a hydrogen vent-flare system.

The liquid or gas should be piped a safe distance from the work and storage areas with flared venting systems. Water pond burning may be used for rapid releases of large quantities as well as relatively long releases. The hydrogen is dispersed through a submerged pipe manifold to evolve into the atmosphere where it is ignited and burned. The water serves as a seal to prevent back mixing of air into the distribution manifold and pipeline and provides some protection for the manifold from thermal radiation damage.

Flare stack exits should provide good corona dissipation and be equipped for weather protection. The lines from LH_2 or SLH_2 systems should be long enough to warm the hydrogen to above liquid-air temperatures (82 K (-312 °F)), preventing liquid-air from flowing back into or around the system and creating a highly oxidizing environment.

5.6.4 Hydrogen Disposal Into Exhaust Systems

Disposal of hydrogen through an exhaust system requires approval of the AHJ. Such approval shall require the hydrogen concentrations in air to be limited to less than 25% of the LFL unless the exhaust system has been designed to contain a hydrogen-air detonation.

5.6.5 Deflagration Venting

Hydrogen-air deflagrations subject to potential confined spaces or closed vessels should be vented to prevent explosions. The maximum deflagration pressure for a given GH₂-air mixture is calculated and an appropriate vent area is provided (NFPA 68). Annex B, Example 3 shows such a calculation.

Explosion vents should not be connected to hydrogen vent systems.

5.6.6 Explosion Prevention

The design, construction, operation, maintenance, and testing of systems for the prevention of deflagration explosions is accomplished by means of one or more of the following methods (NFPA 69):

- Control of oxidant concentration
- Control of combustible concentration
- Explosion suppression
- Deflagration pressure containment
- Spark extinguishing systems

5.7 Contamination

5.7.1 General

The storage and piping systems, including system components, should be designed and installed to allow cleaning of the hydrogen system and effective maintenance of a clean system. Contamination shall be minimized.

5.7.2 Filters

Adequate filters should be used on hydrogen and associated systems. The filter should be placed to effectively collect the impurities in the system and should be accessible for cleaning. Filter elements made of noncalendered woven wire mesh are recommended. Sintered metal elements are not suitable because metal tends to spall and get into the system. As a general rule, the filter element should retain 100% of the particles greater than 150 μ m (0.0059 in.) diameter. Some systems may have more stringent requirements. Provisions for filter isolation and removal of any trapped oxygen or other solid contaminants should be provided.

5.7.3 Interconnected Systems

The arrangement of systems shall be designed so that cleaning or draining practices can be adjusted to ensure dead-end volumes and possible traps are adequately cleaned.

Adequate means should be provided to prevent damage to the lower-pressure system and its components for interconnected systems operating at different pressure levels.

The following protection-related requirements shall apply:

- Pressure-regulating valves, shutoff valves, and check valves do not adequately protect low-pressure systems connected to high-pressure systems. Pressure relief should be in the low-pressure system. The hydrogen supply should be disconnected and capped when the pressure differences in the systems cannot be used in conjunction with relief valves for preventing leakage. Relief valves and burst disks also are required for the protection of third piping systems supplied through valves from the high- or low-pressure system.
- Check valves should not be used when bubble-free tightness is required. Bottled gases have been contaminated when check valves leaked in interconnected systems. Two check valves in series have

been found to be unreliable. Check valves may be used when system contamination is not important and bottle pressures are not permitted to fall within 276 kPa (40 psig) gage of the contaminating pressure. Two shutoff valves with a bleed valve between them should be used if the contaminating pressure exceeds the supply pressure. See Section 5.3.6 for more information.

Explosion hazards in interconnected systems, caused by hydrogen leakage from one system into another, should be prevented by considering the following principles:

- Leakage through valves should always be considered a possibility.
- Overpressurization safety systems should be used for protection.
- The hydrogen supply should be disconnected and capped when the system is not in active use and system pressure differences cannot be used in conjunction with relief valves to prevent unwanted leakage.

Contamination with oxygen, air, or nitrogen may occur from interconnected systems. Check valves should not be relied on to prevent this possible contamination source. Localized concentrations of solid oxygen particles can approach and reach the flammable range. Impurities from the pressurization gas can accumulate in LH₂ during pressurization for transfer operations. Accumulation is less likely when liquid is frequently withdrawn from vessels. Therefore, higher boiling point impurities (everything but helium) will accumulate when liquid is stored and not used and tanks are occasionally topped to make up evaporation losses. The following precautions should be observed:

- Hydrogen liquid should be stored under positive pressure to aid in preventing external contaminants from entering the system.
- The pressurizing gas should be as free as practical of impurities. The levels of impurities, especially oxygen, shall be known to ensure the pressurant gas is satisfactory.
- All transfer and handling equipment for GH₂ and LH₂ shall be clean, dry, and purged.
- Hydrogen should not be recirculated if contamination cannot be prevented.

Permanent liquid storage facilities should be periodically monitored or sampled for build up of condensable impurities.

Hydrogen systems should be maintained under a positive pressure to prevent air, moisture, and particulate contamination when they are not in use.

5.8 Vacuum System

5.8.1 General

A vacuum system is an important tool in maintaining insulating vacuum and purging (removing unwanted hydrogen or other gases from a hydrogen system). The vacuum system can include such components as a vacuum pump (or pumps), valves, instrumentation (vacuum gages), protection from over pressure, and a cold trap.

Important considerations for a vacuum system include flow regimes (laminar or viscous flow, transition or mixed flow, and turbulent or free molecular flow), degree of vacuum (such as rough, high, and ultrahigh), conductance of the vacuum system, pump-down time, materials of fabrication, fabrication techniques to eliminate virtual leaks, seals and gaskets, emissivity of inner surfaces of the vacuum system, and out-gassing of components in the vacuum system.

 GH_2 properties involved in a vacuum system that services GH_2 include (some of these may be related to instrumentation and measurements) GH_2 thermal conductivity, hydrogen ionization efficiency, the gas molecule average velocity, molecular diameter, hydrogen permeation, hydrogen absorption, and hydrogen viscosity.

Vacuum systems should be designed with sufficient volume and necessary system pressure for all required uses throughout the system. Vacuum pumps shall be selected for the highest required degree of vacuum in the system. Pump capacity shall be based on the total calculated peak demand of the system and the pump should meet this peak demand when continuously operating. Multiple pumps shall be installed with the calculated peak demand divided equally among the units when pumps larger than 3.7 kW (5 hp) are required or continuity of service is necessary. Standby pumps should not be installed unless justified by mission criticality. Vacuum vessels should be provided for reserve storage, momentary peak demands, pump pulsation absorption, and entrapment of liquids and other foreign materials that may be introduced into the system. The vacuum vessels should be sized to prevent the pump from cycling too frequently.

5.8.2 Hydrogen Vacuum Pumps

Vacuum pumps used for pumping hydrogen should be rated for hydrogen service.

GH₂ is a difficult gas to pump for a variety of reasons. Vacuum pump considerations include the following:

- The compression ratio of light gases, such as GH₂ and He, is lower than that of the heavy gases for a **diffusion pump** because of their high thermal velocity and small collision cross section. The compression ratio of a diffusion pump for heavy gases will be on the order of 10⁸ to 10¹⁰, whereas, it can be on the order of 10³ to 10⁶ for light gases.
- Modern **turbo-molecular pumps** have high pumping speeds, large hydrogen compression ratios, and low ultimate pressures. The compression ratio is exponentially dependent on rotor speed and the square root of the molecular weight of the gas. The light gases, such as helium and hydrogen, will have compression ratios much smaller than the heavy gases. The speed ratio for argon is about unity for a blade tip velocity of 400 m/s (1,312 ft/s); it is about 3.0 for GH₂. Compression ratios of 1.6 for GH₂ and 4 for argon are obtained for a blade angle of 30° and velocity of 400 m/s (1,312 ft/s). The net compression ratios are calculated to be approximately 100 for GH₂ and 106 for argon if 10 disks (5 rotors and 5 stators) are cascaded. A special blade design for pumping hydrogen is used for optimizing performance. No conventional LN₂ trap is required on a turbo-molecular pump to stop bearing or mechanical pump fluid backstreaming. The compression ratios for all but GH₂, the lightest gas, are high enough that none will backstream from the foreline side to the high vacuum side, provided the pump is rotating at rated angular velocity. An LN₂-cooled surface will not trap the small amount of GH₂ that does backstream into the work chamber because of its low compression ratio (O'Hanlon 1980).
- **Cryogenic pumps** do not handle all gases equally well. The capacity for pumping He and GH₂ is much less than for other gases. Because cryo-surfaces condense vapors, they can accumulate significant deposits able to react with one another or with the atmosphere when warmed. Cryogenic pumps easily pump large amounts of GH₂, have no high voltages, and generate no hydrocarbon, metal film flakes, or other contaminants of their own (O'Hanlon 1980).

 GH_2 will diffuse rapidly in an evacuated space because of average velocity of the gas molecule (average velocity is related to the absolute temperature and the molecular weight). The average velocity for GH_2 is 1,750 m/s (5,741 ft/s), compared to 464 m/s (1,522 ft/s) for air.

A leak in a system being evacuated could result in air being pulled into the system, or gas being pulled in from another part of the system. Consequently, a hydrogen-air mixture could be formed.

Virtual leaks can be reduced by techniques such as using continuous welds inside and intermittent welds outside and avoiding interior screw threads and internal blind holes.

Elastomeric materials used in hoses (such as rubber and Tygon) will absorb and permeate hydrogen readily. Thus, the length of such hoses should be minimized.

The exhaust of rotary mechanical pumps should be vented outside of a building because of oil vapors in the exhaust (an oil mist separator may be used to reduce the oil vapor in the exhaust, but it does not adequately remove all the oil vapors). The vent line should not run vertically from the exhaust connection because water or other vapors that have condensed on the cooler walls of the vent line will drain into the pump and contaminate the fluid. This problem may also be addressed by the addition of a sump at the exhaust connection to collect the vapors before they can flow into the pump.

Condensation on the interior walls of rotary piston and rotary vane vacuum pumps can occur when large quantities of water or other condensable vapors are being pumped. Gas (usually room air) is admitted through a ballast valve to avoid condensation and its resulting problems. The ballast valve is positioned to allow the ballast gas (which can be as much as 10% of the pump displacement) to enter the chamber during the compression stage. This could result in the creation of a combustible mixture within the pump when a system containing hydrogen is evacuated.



6 Hydrogen and Hydrogen Fire Detection

6.1 Hydrogen Detection

6.1.1 General

The system design should ensure that detection occurs immediately and operating personnel are notified as appropriate if hydrogen leaks into the atmosphere or a hydrogen fire occurs.

GH₂ is colorless and odorless and normally not detectable by human senses. Means shall be provided to detect the presence of hydrogen in all areas where leaks, spills, or hazardous accumulations may occur.

A hydrogen detection system must be compatible with other systems such as those for fire detection and fire suppression. The detection units should not be ignition sources. Total times for detection, data summary, transmission, and display should be as short as possible. A portable hydrogen detector should be available.

Well-placed, reliable hydrogen detectors are imperative for safe installation. Continuous automatic sampling equipment with sample points strategically located should be provided as needed. The sampling equipment shall be calibrated to provide for short response times and detection of at least 25% of the LFL. Detection of LH₂ or SLH₂ leaks by observation alone is not adequate. Although a cloud of frozen air and moisture may be visible, such a cloud is not a reliable sign of a hydrogen leak because clouds of water vapor also rise from cold, exposed surfaces when no hydrogen leak is present.

The number and distribution of detection points and time required to shut off the hydrogen source should be based on factors such as possible leak rates, ventilation rates, and the volume of space for an interior location. The detection signal also should actuate warning alarms and automatically effect shutoff whenever practicable.

Considerations for the design of a reliable hydrogen detection and monitoring system follow.

- Evaluate and list all possible sources to be monitored (valves, flanges, connections, bellows, etc.) and provide valid justification for sources not monitored.
- Evaluate the expected response time of the leak detection system to ensure compatibility with the responding safety system.
- Provide visual and audible alarms as necessary when the worst allowable condition (red line) is exceeded. The allowable condition must still be in the safe range, but a warning indicates a problem.
- Provide portable detectors for field operations or isolated areas and permanently installed detectors for remotely automated operations.
- Use a program to maintain and periodically recalibrate detectors to ensure acceptable performance.
- Determine the number and distribution of sampling points in the hydrogen detection system based on the possible leak rate, ventilation amount, and area size. Consideration should be given to methods of routing hydrogen to the detector.

The appropriate hydrogen detection system should be used when explosion suppression techniques using inert gas purges are installed (NFPA 69). The possibility of oxygen deficiency must be considered when purge gases are used.

Tables A6.1, A6.2, and A6.3 give information on hydrogen gas detectors. Table A6.1 shows a list of typical GH_2 detectors. Table A6.2 shows a survey and analysis of commercially available hydrogen sensors. Table A6.3 shows sensitivity limits of hydrogen detectors.

6.1.2 GH₂ Detection Specifications

Detection and alarm at 1% by volume hydrogen concentrations in air, equivalent to 25% of the LFL, is required for enclosed areas in which GH_2 buildup is possible (29 CFR 1910.106). Detection and alarm at 0.4% by volume hydrogen concentrations in air (equivalent to 10% of the LFL) is required for permit-required confined spaces (29 CFR 1910.146).

It may be necessary to conduct a gas sample through a sensing line to the sensor under conditions in which the sensor cannot be located at a leak source. The response time under such conditions depends on the length of the sensing line. Response times should be 1 s or less if possible.

A 1% by volume hydrogen concentration in an exhaust purge should generate an alarm. A higher hydrogen concentration at a purge exhaust indicates a major leak or a fire hazard after the purge is exhausted in air.

A 1% by volume hydrogen concentration should generate an alarm in a vacuum chamber when it is not evacuated and at anytime in the evacuation duct.

A 1% by volume hydrogen concentration at any point 1 m (3.28 ft) from the hydrogen equipment should generate an alarm in areas around hydrogen facilities. The performance of the detectors depends on the location of sensors and the leak and wind directions, and they may fail to indicate a leak. A larger number of sensors may be necessary to survey the area of concern.

Specifications for hydrogen sensors should include requirements for the following:

- Minimum gas concentration detection requirements
- Full scale range of the detector system
- Level of concentration for which alarm detection is required
- Response time of the detector system
- Accuracy of sensors
- Reliability and recalibration frequency
- Interface to facility safety and shutdown systems

6.1.3 Detection Technologies

Bubble testing is one of the simplest methods of leak detection; however, it is not a continuous monitoring system, it needs to be applied directly on the source of the leak, it can only be used with inert gases at low pressure, and it is limited to temperatures above freezing. Bubble solutions can detect very small leaks but do not measure concentrations.

Catalytic combustion sensors detect hydrogen gas by sensing the heat generated by the combustion of hydrogen and oxygen on the surface of a catalytic metal such as palladium or platinum. The sensors work well for detection of hydrogen in the 0% to 4% by volume (0% to 100% LFL) in air but do not operate in inert environments or 100% by volume hydrogen. Sampling systems can be designed to mix air with the sample before exposure to the catalytic sensor for operation in inert environments; however, this results in a longer response time. Catalytic sensors such as sintered bronze utilize a heated filament and need to be enclosed in flame arrestors to prevent the sensors from becoming ignition sources. Also, catalytic sensors are not hydrogen specific and will respond to other combustible gases such as methane.

Thermal conductivity sensors work well in stable environments with minimal temperature variations and a constant background gas. Thermal conductivity sensors work well in background gases that have a thermal conductivity that varies significantly from hydrogen, such as air or nitrogen. However, they do not work in helium backgrounds — a significant drawback for LH₂ systems, as helium purges are often

required because helium does not solidify at LH₂ temperatures. Thermal conductivity sensors can go from 0.02% to 100% by volume hydrogen detection.

Electrochemical sensors typically utilize a liquid electrolyte and require a gas permeable membrane for the hydrogen to reach the electrolyte. The sensors are low power and can operate from 0.02% to 100% by volume hydrogen. Exposure of the membrane to cryogenic or time-varying temperatures greatly affects the gas diffusion and can make the sensor unreliable.

Semiconducting oxide sensors rely on surface effects with a minimum oxygen concentration present and do not work in inert environments. Semiconducting oxide sensors can operate at lower powers than catalytic sensors, but performance at lower temperatures is degraded. Semiconducting oxide sensors are relatively new and not as common as the older catalytic based systems.

Mass spectrometers are extremely sensitive (1 ppm), very specific to the gas being detected, linear over a wide dynamic range, and provide continuous monitoring. The complexity and high cost of mass spectrometers requires skilled operators and the use of sampling systems to monitor multiple locations with one instrument. The use of long sample lines can significantly reduce the response time.

Gas chromatographs are similar to mass spectrometers in their sensitivity and accuracy; however, measurement times are extremely slow. Gas chromatographs are typically used in a laboratory to analyze the gas collected in the field with sample bottles.

Ultrasonic leak detection can be used when hydrogen specificity is not required and there is minimal background interference noise. Ultrasonic systems typically are used to pinpoint the source of a leak, and cannot measure whether a combustible mixture is present.

Glow plugs and heat sensors are less common techniques used for rapid leak detection. The glow plugs ignite any combustible mixture present, and a heat sensor detects the fire and provides rapid shutdown of the process. The theory is that it is better to burn the hydrogen gas than let a combustible mixture accumulate, and the facility can shut down before the fire can do significant damage.

Other methods by which LH₂ leaks can be detected include loss of vacuum, the formation of frost, the formation of solid air, or a decrease in outer wall temperature on vacuum-jacketed equipment.

6.1.4 Hydrogen Detector Installation and Use

Illustrations of how different types of hydrogen detectors may be used in various applications are given below.

6.1.4.1 Launch and Ground Test Facilities

Use catalytic sensors detecting over a 0% to 4% (0% to 100% of LFL) range for sampling in cryogenic and gas transfer systems.

Use mass spectrometers detecting 0.01% to 10% of the LFL for sampling purged enclosures.

Use catalytic or semiconductor oxide sensors with air mixing detecting over a 0% to 4% (0% to 100% of LFL) range as portable sniffers.

Use gas chromatography, which has parts-per-billion-by-volume capability, for the detection of hydrogen in purged lines and vessels through the use of samples collected in sample bottles.

Take samples in sample bottles at various times during ascent of flight systems and analyze the samples after flight using a gas chromatograph.

Monitor the atmosphere of indoor laboratories by using catalytic sensors detecting over a 0% to 4% (0% to 100% LFL) range. However, various chemicals (such as room temperature vulcanizing adhesives) in an indoor environment can poison catalytic sensors; consequently, another type of hydrogen detector should be considered for use in such an environment.

6.2 Hydrogen Fire Detection Systems

6.2.1 Hydrogen Fire Detection

A fire detection system should be capable of detecting, at a minimum distance of 4.6 m (15 ft), the flame from the combustion of 5.0 L/min (0.18 ft 3 /min) of GH $_2$ at NTP flowing through a 1.6 mm (0.0625 in.) orifice to produce a 20 cm (8 in.) high flame. For a potential release of a large volume of hydrogen, sensors with the ability to detect flames at distances greater than 4.6 m (15 ft) should be used to provide coverage over a large area.

The fire detection should not be susceptible to false alarms from the sun, lightning, welding, lighting sources, and background flare stacks.

The fire detection system response time should meet the requirements for the specific application for prevention of loss of facility, equipment, and protection of personnel.

Fixed systems are required for continuous monitoring of remote operations and portable systems are required for field operations.

Special imaging systems are required for determining the size and location of a flame for assessment of the hazard because hydrogen flames are not visible during daylight conditions.

Table A6.4 gives information on hydrogen fire detection. Figures A6.1 through A6.4 provide additional information on optical detection and flame emission properties. Figure A6.1 gives irradiance of common IR sources. Figure A6.2 gives atmospheric IR transmission and GH₂-air flame emission. Figure A6.3 gives ultraviolet (UV)/visible (VIS)/near-IR emissions. Figure A6.4 gives GH₂-air flame components.

The solar-transmission-emission-detector sensitivity trade-off considerations are as follows:

- Solar: The radiation from the sun can overpower the hydrogen flame emission resulting in an invisible flame during the day (in the visible spectrum).
- Transmission: A large percentage of the radiation emitted from a hydrogen fire originates from the hot water molecule. Emission peaks occur at the same location water (humidity) in the atmosphere absorbs radiation.
- Emission: Hydrogen fires tend to emit over a broad range and are not characterized by extreme peaks such as the 4.3 x 10⁻⁶ m (1.4 x 10⁻⁵ ft) peak for hydrocarbon fires.
- Detector Sensitivity: Different types of detectors are sensitive to different parts of the spectrum. A
 higher sensitivity detector at a smaller emission peak may outperform a less sensitive detector at a
 larger emission peak.

6.2.2 Hydrogen Fire Detection Technologies

Thermal fire detectors classified as rate-of-temperature-rise detectors and overheat detectors have been manufactured for many years and are reliable. Thermal detectors need to be located at or very near the site of a fire.

Optical sensors for detecting hydrogen fires fall into two spectral regions — UV and IR. UV systems are extremely sensitive; however, they are susceptible to false alarms and can be blinded in foggy conditions. IR systems typically are designed for hydrocarbon fires and are not very sensitive to hydrogen fires.

Imaging systems are mainly available in the thermal IR region and do not provide continuous monitoring with alarm capability. The user is required to determine if the image being viewed is a flame. UV imaging systems require special optics and are very expensive. Low-cost systems, using low-light silicon charge coupled device (CCD) video technology with filters centered on the 940-nm and 1,100-nm emission peaks, have been used at some facilities.

A **broom** has been used for locating small hydrogen fires, because a dry corn straw or sage grass broom easily ignites as it passes through a flame.

A **dry fire extinguisher** or throwing **dust** into the air also causes the flame to emit visible radiation. This technique should be used with care in windy, outdoor environments in which the light hydrogen flame can easily be blown around.

6.2.3 Hydrogen Fire Detector Installation and Use

Illustrations of how different types of hydrogen fire detectors may be used in various applications are given below.

6.2.3.1 Launch and Ground Test Facilities

Use thermal protect-o-wire, temperature sensors, and UV-only optical fire detectors for transfer systems.

Use thermal (8 μ m to 12 μ m), mid-IR (2.7 μ m), and near-IR (940 nm and 1,100 nm) imaging; UV imaging systems (280 nm); and heat sensing devices for launch operations, and rocket engine testing.

6.2.3.2 Flight Systems

Use fire detection equipment as determined appropriate by the AHJ for flight systems.

6.2.3.3 Indoor Laboratories

Indoor laboratories use appropriate, commercially available equipment.

7 Operating Procedures

7.1 General Policy

The best single investment in safety is trained personnel following approved operating procedures, standards, and guidelines.

7.1.1 Personnel

Full consideration for the safety of personnel at and near hydrogen facilities should start in the earliest planning and design stages. Safety documentation made available to personnel should describe the safety organization and comment specifically on inspections, training, safety communications and meetings, operations safety and instruction manuals, accident investigations, and safety instruction records. Training should familiarize personnel with the physical, chemical, and hazardous properties of the cryogens and the nature of the major process systems of the facility, in accordance with 29 CFR 1910.120. The buddy system (two qualified personnel shall be present) must be followed when required. No more than the minimum personnel necessary should be present in a hazard area.

7.1.2 Standard Operating Procedures

Standard operating procedures (with checklists as required) shall be developed for all hydrogen operations (29 CFR 1910.103; NFPA 50A and 50B). All hydrogen standard operating procedures shall be reviewed periodically for observance and improvement, and approved by the AHJ. Safety is achieved while working with hydrogen by adhering to the following principles:

- Prevent hydrogen leaks
- Keep constant watch to immediately detect accidental leaks and take proper action
- Prevent accumulations of leaked hydrogen using plentiful ventilation
- Eliminate likely ignition sources and suspect unknown ignition sources
- Ensure safe operation of cryogenic systems through periodic leak and flange joint torque checks
- Always assume hydrogen is present, and verify the system has been purged to less than 1% when
 performing system maintenance on a hydrogen system. Always assume oxygen is present and verify
 the system has been purged to the appropriate level when reintroducing hydrogen into a system.

7.1.3 Special Operating Procedures

Special operating procedures should be developed, and these shall be approved by the AHJ, to counter hazardous conditions when the design and use of safety equipment do not reduce the magnitude of an existing or potential hazard. The procedures should be verified by demonstration tests.

7.1.4 Repairs, Alterations, and Cleaning

Repairs, alterations, cleaning, or other operations (especially those performed in confined spaces in which hydrogen vapors or gases are likely to exist) should have an approved safety procedure. As a minimum, the safety procedure shall include the evacuation or purging requirements necessary to ensure safe entry as well as the maximum flammable limits allowed of 25% of the LFL in the confined space. The limit is 10% of the LFL in a permit-required confined space. Personnel engaged in the operations shall be advised of the hazards that may be encountered, and at least one person shall be immediately available while the work is being performed to administer emergency rescue, should it be necessary. An attendant shall be available for work in a permit-required confined space (29 CFR 1910.146).

7.1.5 Modifications, Repairs, or Decommissioning

Before modifications, repairs, or decommissioning, cryogenic vessels should be drained, warmed to ambient temperature, purged and sampled, and all pipelines disconnected or flanged and tagged. Disconnected lines should have blank flanges with gaskets to prevent the leak or spill of hazardous materials near the vessel. Any electric power supply to equipment within the vessel should be deenergized. Vessels placed in standby condition should be maintained under a positive pressure of dry gaseous nitrogen (GN_2) .

The vacuum annulus should be warmed and purged with dry GN_2 , and the purge supply should be sufficient for warming the insulation to remove absorbed moisture or other gases for major repairs or modifications. Warm-nitrogen purge rates of 4 to 7 m³/min·m³ (4 to 7 ft³/min·ft³) of insulation should be sufficient. Approved procedures shall ensure that inert gas purging does not result in a potential asphyxiation hazard to personnel. Purging is more effective when a sparger arrangement of small breathers is located at the bottom of the casing. Do not use He to purge a vacuum annulus because of the difficulty of removing it from the annulus. Do not use GN_2 to purge a vacuum annulus if the temperature of the inner vessel is sufficiently low to condense the GN_2 .

7.1.6 Contamination Control

7.1.6.1 General

Cleaning procedures should be established and a method of effective contamination controls developed to maintain the hydrogen systems to the cleanliness levels required. The procedures shall protect personnel from exposure to toxic chemicals or environments in which asphyxiation could occur. Effective cleaning removes greases, oils, and other organic materials as well as particles of scale, rust, dirt, weld spatter, and weld flux.

LH₂ or SLH₂ exposed to air can form a slurry of solid oxygen and nitrogen which tends to be richer in oxygen than air. Solid contaminants can contribute to the generation of static electricity in flowing systems and should be held to a minimum. Filter elements in LH₂ servicing systems should be regenerated well before their capacity is reached. Explosions have occurred in filters contaminated with solid air. The warm-up and purge of LH₂ transfer systems usually accomplishes the regeneration of filters. SLH₂ systems require special considerations because of the presence of solid hydrogen particles. For example, a filter that would trap solid hydrogen particles should not be used in a SLH₂ transfer system.

Complete systems may require disassembly for suitable cleaning. Components that could be damaged during cleaning shall be removed and cleaned separately. The cleaning of multiple-branch piping systems should be integrated into the sequence of construction operations.

It is necessary to determine or estimate the nature, possible locations, and quantities of contaminants present to choose the most practical method of cleaning, the level of cleanliness, the inspection procedures, and the testing for each group of cryogenic fluids. The fluid operating levels including temperature and pressure may also affect the cleanliness level desired. Passage arrangement also should be studied so cleaning, washing, or draining practices can be adjusted to be sure dead-end passages and possible traps are adequately cleaned.

The compatibility of cleaning agents with all construction materials must be established before use. The cleaning methods include steam or hot-water cleaning, mechanical descaling, vapor degreasing, solvent degreasing (washing), detergent degreasing (alkaline washing), acid cleaning (pickling), and purging.

Note: The choice of organic cleaning solvents and associated procedures is currently being reviewed and modified. The organic solvent of choice has been chlorofluorocarbon 113 (trichlorotrifluoroethane, Mil-C-81302, Amendment 1, type II), because it is an ideal solvent for performing particle count and nonvolatile residue analysis. It is also nonflammable and relatively nontoxic. Production of chlorofluorocarbons currently is restricted and is being phased out because the release of the compounds into the atmosphere damages the environment.

Alternative cleaning solvents are being developed and investigated and probably will come into use in the near future. Alternative cleaning solvents include the new hydrochlorofluorocarbons (HCFC), deionized (DI) water, and isopropyl alcohol (IPA). The effects of these changes on the cleaning of hydrogen systems have not yet been assessed.

A recommended cleaning procedure for hydrogen systems follows:

- 1) All loose particles such as sand, grit, rust, and weld splatter should be removed from a warm system by flushing the system or component with an approved solvent to degrease and dry it. The system should then be flushed a second time with demineralized water.
- 2) The system should be dried by evacuation or by flowing dry nitrogen gas through it. See 4) below if the system cannot withstand a vacuum. The system should be cold-shocked with LN₂ to break loose attached particles. The quantity of LN₂ used should not exceed the weight limit of the vessel if LN₂ cold-shock is used to break loose attached particles. The particles can be flushed out with LN₂ flowing through filters. The filters should be cleaned separately.
- 3) Systems should be dried by three cycles of evacuation and purging through a cold trap before filling with hydrogen gas. Three cycles usually will dry a system so the cold trap should show no further collection.
- 4) The system may be dried by flowing hot nitrogen gas through it if the system cannot withstand a vacuum. The nitrogen gas temperature should be sufficient to remove water, but should not be too hot for the insulation material.
- 5) Cleaning fluids shall be disposed of according to appropriate procedures.

Flexible hoses used should be sealed and assurance indicated that certified cleanliness has been maintained. The ends of the hoses should be closed with metal caps, covered with a clean plastic bag or sheet, and sealed with tamperproof seal tape as required.

The frequency at which filters should be cleaned depends on the amount of use and impurities in the fluid. Operators watch increases in pressure drops and clean filters as needed. Filters are cleaned by disconnecting, warming, draining, flushing with an approved solvent or ultrasonic cleaning, and thoroughly drying. Filters must not be cleaned by back-flushing through the system.

7.1.6.2 Decontamination

A vessel should periodically be decontaminated by draining its contents and letting the product container warm to permit removal of all contaminants. The warm-up schedule is determined from the service history. Experience shows that contamination occurs in frequently filled and emptied roadable dewars. Large fixed dewars that are not often filled and emptied do not require frequent decontamination unless they have been subjected to a contaminating condition. The interval depends on the degree of contamination and shall be determined by the AHJ.

The container should be vacuum purged (if strong enough to withstand a vacuum of 1.33 kPa (10 torr)) to ensure decontamination. A warming or pressure purge is necessary if the dewar is not strong enough.

7.1.7 Hazards of Substituting Dewars

 LH_2 and liquid helium dewars, as ordinarily constructed, may not be strong enough to hold LOX, liquid air, or LN_2 because of the structural weakness of the vessel.

Hydrogen and helium equipment can be used interchangeably, although it is not recommended. No other substitutions are permitted without approval by the AHJ. The contents must be accurately marked on the vessel and its contents sampled for contamination in all cases.

7.1.8 Protective Clothing

All personnel working with LH_2 or SLH_2 who may be exposed to cryogenic vapors shall have eye and hand protection. Face shields are required when operating any hydrogen system under pressure and connecting or disconnecting lines or components. Systems should be designed and operated to reduce potential for unprotected personnel coming in contact with uninsulated piping or vessels containing cryogenic hydrogen.

Properly insulated gloves should be worn when handling anything that comes in contact with cryogenic liquids or vapors. Gloves should fit loosely and remove easily. Adequate foot protection should be provided, and the trousers should be worn outside boots or work shoes. Open or porous shoes are not permitted. Any clothing splashed, sprayed, or soaked with fuel vapors or oxidizers shall be removed until completely free of the gases.

Personnel should avoid wearing clothing made of nylon or other synthetics, silk, or wool because these materials produce charges of static electricity that can ignite flammable gas mixtures. Ordinary cotton, flame-retardant cotton, or NomexTM (or the equivalent) clothing is preferred. Gauntlet gloves, tight clothing, or clothing that holds or traps liquid against the body must be avoided.

Hard hats should be worn as appropriate. Hearing protection shall be utilized as appropriate.

Personnel shall be provided appropriate protective clothing during cleaning or decontamination operations.

7.2 Storage and Transfer Procedures

7.2.1 LH₂ Off-Loading

The procedures for off-loading LH₂ at facilities should include notification of the safety department or safety representative of the location, time, and amount of LH₂ to be off-loaded. The safety representative shall verify that a preoperation briefing has been conducted and approved procedures are used, emergency escape routes are clear, and the operational area is clean and free of combustible materials and ignition sources.

Contractor unloading procedures, vehicle schematics, and descriptions of the piping systems that interact with a facility should be provided by the contractor to better determine the facility design and necessary precautions and procedures during and after unloading operations.

A checklist should be made of the operations to be performed by the supplier and user of the LH₂. No LH₂ transfer should begin unless there is a positive remote shutoff capability in the trailer or other supply vehicle system. This is necessary to protect the unloading area if a leak or spill occurs.

7.2.2 Purging

The major step to be taken before loading a LH_2 vessel is to ensure the removal of any condensable gas from the transfer line and vessel, as appropriate. Condensable gas trapped in the vessel or transfer line can solidify and can introduce a potential fire and explosion hazard. Annex B, Example 10 analyzes the purging of a vessel.

Air in a system must be purged prior to putting hydrogen in the system. Likewise, hydrogen must be purged from a system before it is opened to make repairs or do maintenance, for example. Three purge techniques are flowing gas, pressurizing-venting cycle, and vacuum purge.

A flowing gas purge is least likely to ensure a positively purged system. It requires the use of an inert gas flowing into one part of the system and flowing out another part of the system. Considerations include the volume to be purged, gas flow rate, dead ends, and purge duration. Turbulent flow should be achieved or the flow rate should be sufficiently high that all parts of the system are thoroughly purged. It is important that all voids or dead legs be adequately purged.

- A pressurizing-venting cycle purge requires alternate pressurizing and venting of the system to progressively dilute air until a safe atmosphere is obtained. Air in the system is diluted with an inert gas (helium) to a positive pressure within the working pressure range of the vessel. The mixture is displaced by venting to the atmosphere. The system is repressurized with helium to the positive pressure, and the mixture is again vented to the atmosphere. A positive pressure must be maintained in the receiver during these procedures to prevent the backflow of air. An analysis for residual air in the system is a desirable means of verifying the completeness of the purge. LH₂ can now be slowly introduced into the container.
- Vacuum purging requires fewer operations and produces a uniform concentration throughout the
 system. It is done by venting the system to atmospheric pressure, evacuating to a relatively low
 pressure (1.33 kPa; 10 torr), repressurizing the system with an inert gas to a positive pressure, and
 again venting to atmospheric pressure. The operator must be sure the container or system will not
 collapse when a vacuum is applied and air does not leak into the system when it is under a vacuum
 during vacuum purging.

Vacuum purging may be accomplished as follows:

- The use of inert gas before hydrogen.

The system is initially evacuated, to 1.33 kPa (10 torr), for example. The system is tested under static conditions to ensure it is tight, by observing the rate of pressure rise within the system. Nitrogen, or helium if necessary, is introduced to atmospheric pressure. The system is re-evacuated to 1.33 kPa (10 torr). The system is ready for hydrogen gas.

- The use of hydrogen gas.

The use of hydrogen gas is similar to the use of inert gas before hydrogen, except the inert gas step is omitted. The system is purged with hydrogen gas and evacuated for three complete cycles, after initial evacuation, to 1.33 kPa (10 torr).

The use of inert gas before air.

The use of inert gas before air is for purging GH_2 from a system. This may be accomplished as follows:

- The system initially is evacuated, to 1.33 kPa (10 torr) for example.
- Nitrogen, or helium if necessary, is introduced to atmospheric pressure. The system is reevacuated to 1.33 kPa (10 torr). The system is ready for air.

New vessels containing air usually are purged with nitrogen or helium gas until the oxygen concentration, as measured from the vent system, is below 1% by volume (CGA G-5.4). Hydrogen gas at ambient temperature is used for purging the nitrogen from the system.

Any liquid remaining in vessels containing LH₂ or cold hydrogen vapor may be removed through the liquid transfer hose to a liquid disposal system or allowed to boil off through the hydrogen pressure buildup coil.

7.2.3 Loading Operations

Storage and transport vessels must be purged with an inert gas before the vessels are loaded. Over-the-road trailers can be pressurized to about 241 kPa (35 psig) gage and allowed to stand for 30 min before they are checked for leaks. The inert gas should be released through the vent system, maintaining about 3.4 kPa (0.5 psig) gage in the trailer. The oxygen content in the vented purge gas should be less than 1% by volume before the GH_2 is introduced (CGA G-5.4).

Liquid level and sampling considerations include the following:

- The procedures for filling LH₂ trailers and storage vessels must be controlled to prevent overloading.
 Overloading the vessels reduces the ullage space and may not only result in LH₂ leakage during transportation (for trailers), but could also cause unwarranted thermal cycling and result in the relief valves becoming inoperable.
- Composition acceptance tests should be performed on LH₂ in accordance with specification Mil-Prf-27201 and ASTM F310-70 before it leaves the filling site. The contents of storage and transport vessels engaged in continuous service also shall be sampled as required by the AHJ. The residual products in trailers, railroad cars, or barges irregularly used should be sampled and analyzed before loading and at arrival at the filling site (Mil-Prf-27201).

Concerns related to LH₂ transfers include the following:

- Dewars shall be connected to an appropriate electrical ground that is verified periodically. The dewars generally shall be inspected for leaks or mechanical defects and checked for pressure and vacuum. The connections should be cleaned and purged. Contamination should be avoided.
- Surfaces should be watched for condensed water because it indicates leaks or a deficiency in insulation. A leak check with a portable detector should be made after each assembly or alteration. An approved lubricant for O-rings should be used.
- All transfers should be made in tightly closed systems. LH₂ should not be transferred into an openmouthed dewar or allowed to come into contact with air, because it can become contaminated with solid air.
- Ground wires should be securely clamped across each coupling before transfer. The ground wires should be connected before the coupling is mated.
- All fuel transfers should be made against enough backpressure to prevent air migration.
- GH₂ and LH₂ shall not be transferred in electrical storms or if there is a fire near the facility. If begun, the transfer shall be terminated as directed by the AHJ.
- Dewars and gas trailers should be disconnected from the test equipment after the transfer operation
 and moved away from the test facility as soon as practical. Dewars may remain connected between
 research operations at the discretion of the test conductor in controlled areas where large dewars are
 used and disconnection may constitute a hazard. Movements of dewars and tube trailers should be
 avoided during peak traffic hours.

Checklists are substantial aids to safe operations and are required for all except the most simple installations. There should be checklists of items concerned with safety of the test room and test area in addition to checklists of items pertaining to specific equipment. The checklists shall contain such items as combustible gas detection, ventilation, de-energizing of electrical ignition sources, posting of warning signs, and notification to plant protection and central control and other organizations listed by the AHJ.

7.2.4 Cool Down of Cryogenic Systems

During a cool down, cryogenic systems can experience large circumferential and radial temperature gradients that give rise to stresses not present during steady-state operation. Liquid flow cools a pipe faster than comparable gas flow, and the possibility exists for nonuniform cooling of pipes when two-phase flow occurs.

The largest circumferential temperature gradients, and consequently the highest added stresses, occur during stratified two-phase flow. Stratified two-phase flow occurs when liquid flows along the bottom or outer radius of a pipe or bend, and gas flows along the top or inner radius. Such conditions have caused significant pipe bowing in large cryogenic systems. Stratified flow has been found to decrease with increasing flow rate. During cool down, a minimum flow rate should be maintained to avoid pipe bowing.

Too rapid cooling can also cause large radial temperature gradients by quickly cooling the inner wall of sections, such as thick-walled flanges, while the outer wall remains near ambient temperature. Annex B, Example 9 analyzes the flow rate that should not be exceeded to avoid excessive cooling rates.

It is recommended that cool down be accomplished by introducing a cold gas into the pipe, as from a vaporizer, instead of a liquid. Cooling with cold gas is always recommended for large cryogenic systems. Another alternative is the liquid soak, in which a small amount of cryogenic liquid is introduced into a limited portion of the piping system and allowed to evaporate under very low-, or no-flow, conditions so cooling occurs mostly by means of cold gas.

The margin of safety between the recommended cool down safe-flow limits and the limits at which pipe failure will occur is not well established, but operation of large systems within recommended limits has verified their safety.

Quantitative guides have been developed to maintain circumferential and radial temperature gradients within proven safe limits throughout cool-down for particular cryogenic liquids contained in horizontal pipes of particular common materials. The following guides to safe cool down rates should be followed:

- Thermal stress problems on cooldown are most likely in long (length to diameter (L/D) > 100), thick-wall pipes with thick flanges.
- Figure A4.4 shows the minimum LH₂ and LN₂ flow rates that must be maintained to avoid wave or stratified flow (Liebenberg et al. 1967).
- Figure A4.5 shows the maximum LH₂ and LN₂ flow rates to avoid excessive thermal stress from rapid cooling of the thick-wall piping sections such as flanges (Novak 1970).
- A steady cooldown flow rate of LH₂ or LN₂ that not only avoids stratified flow but keeps the maximum cooldown stress within the allowable stress range may not be possible for pipelines and flanges of certain sizes and materials. A pipeline in which this condition exists may be precooled with gas or slugs of liquid (Novak 1970). See Section 7.2.2 on Purging.

Annex B, Example 9 examines flow rates during cool-down.

An optional method of preparing a warm vessel or system to receive LH_2 uses LN_2 for precooling. The cooling process evaporates large amounts of the cooling liquid. This may become a hazard if the cooling liquid is hydrogen. Perform the following before LH_2 is introduced to the vessel or system:

- 1) Evacuate the vessel or system to approximately 1.33 kPa (10 torr). A warm, inert gas pressure purge should be carefully planned as a special case if this vacuum cannot be tolerated.
- 2) Introduce LN₂ into the vessel or system, taking care to prevent air migration that will cause contamination. Care should be taken to consider the extra weight of LN₂ because of its density, which is more than a factor of ten greater than the density of LH₂.
- 3) Allow ample time to obtain all of the cooling possible from the liquid and the cold gas. Drain off the remaining LN_2 and remove the nitrogen atmosphere by evacuating the vessel.

8 Transportation

8.1 General

Standards and guidelines for the transportation of hydrogen are for the protection of people, buildings, roads, and equipment.

8.1.1 Public Thoroughfare

Transportation of GH_2 or LH_2 on a public thoroughfare is covered by Federal DOT (49 CFR) and state transportation requirements. The transport of GH_2 or LH_2 shall adhere to these requirements. A brief summary of 49 CFR is provided in Appendix D.

8.1.2 Private Thoroughfare

Transportation of GH₂ or LH₂ on a thoroughfare that is privately controlled is the responsibility of the AHJ. Such transportation shall meet the appropriate federal and state labor standards and guidelines in addition to standards imposed by the AHJ.

8.1.3 DOT Definitions

Materials transport containers are described according to the following definitions developed by the DOT:

- GH₂ is specified as a compressed gas (package shipping identification number UN (United Nations) 1049) with a hazard class of 2.1 (flammable gas) by DOT (49 CFR 172.101 and 49 CFR 173.115).
- LH₂ is specified as a cryogenic liquid (package shipping identification number UN 1966) with a hazard class of 2.1 (flammable gas) by DOT (49 CFR 172.101 and 49 CFR 173.115).
- Cargo tank (49 CFR 171.8) is bulk packaging that meets the following criteria:
 - A tank primarily intended for the carriage of liquids or gases that includes appurtenances, reinforcements, fittings, and closures (for "tank," see 49 CFR 178.345, 49 CFR 178.337, and 49 CFR 178.338, as applicable).
 - It is permanently attached to or forms a part of a motor vehicle; or is not permanently attached to a motor vehicle but by reason of its size, construction, or attachment to a motor vehicle is loaded or unloaded without being removed from the motor vehicle.
 - It is not fabricated under a specification for cylinders, portable tanks, tank cars, or multiunit tank car tanks.

A cylinder is a pressure vessel with a circular cross section designed for pressures greater than 275.7 kPa (40 psia) (49 CFR 171.8).

8.2 Transport on Public Thoroughfares

8.2.1 General

While most hydrogen commerce on public thoroughfares involves commercial carriers, the responsibility for complying with federal and state transportation laws rests not only with them but also with the organizations that receive and handle hydrogen.

8.2.2 Training

Personnel involved in handling, receiving, shipping, and transport of a hazardous material shall receive appropriate training (49 CFR 172 Subpart H).

8.2.3 Emergency Response

During all phases of transport, emergency response information is required at facilities where hazardous materials are loaded, stored, or handled (49 CFR 172 Subpart G). Advanced planning for a variety of potentially hazardous and disastrous fires and explosions shall be undertaken with full realization that the first priority is reduction of risk to the lives of emergency personnel and bystanders. A hydrogen MSDS contains useful emergency response information and shall be available on site. Shipments of hydrogen may be monitored by CHEMTREC at 1-800-424-9300. Other emergency information sources include the Dow Chemical USA Distribution Emergency Response System at 1-517-634-4400 and the Union Carbide Corporation Hazardous Emergency Leak Procedure (HELP) that provides information 24 hours a day at 1-304-744-3487. Note that the above phone numbers are current as of the time of publication, but are subject to change.

8.2.4 Transport Requirements for GH₂

49 CFR gives packaging requirements for the various GH₂ container types. Annex D gives a summary of packaging sections of 49 CFR. 49 CFR 172.101 and 49 CFR 173 give general requirements for the transport of GH₂, such as the following:

- Packaging must be labeled or placarded.
- GH₂ cannot be transported aboard passenger aircraft, railcars, or ships. Up to 150 kg (331 lb) are permitted aboard cargo aircraft. It may be stowed above or below deck aboard a cargo ship away from chlorine gas and living quarters in accordance with 49 CFR172.101.

8.2.5 Transportation Requirements for LH₂

49 CFR gives packaging requirements for the various LH₂ container types. Annex D gives a summary of packaging sections of 49 CFR. 49 CFR 172.101 and 49 CFR 173 give general requirements for the transport of LH₂, such as the following:

- Packaging must be labeled or placarded.
- LH₂ is not permitted aboard passenger aircraft, passenger railcars, or cargo aircraft. It may be stowed only above deck on cargo ships away from living quarters in accordance with 49 CFR 172.101.

8.2.6 Security Requirements for Hydrogen Transportation

Recently enacted 49 CFR Part 172, Subpart I (2003), "Security Requirements for Offerors and Transporters of Hazardous Materials" established new requirements for shippers and carriers of certain hazardous materials to develop and implement security plans to enhance the security of Hazardous materials (HAZMAT) transported in commerce. 49 CFR 172.800 gives general requirements applicable to the transport of GH2 and LH2, such as the following:

- Development and implementation of plans to address security risks related to the transportation of hazardous materials
- Personnel security; background investigation and training
- Applicability: bulk packaging having a capacity equal to or greater than 13,248 L (3,500 gallons) for liquids or gases

8.3 Transport on Privately Controlled Thoroughfare

8.3.1 Standard Commercial Operation on Site

Federal and state transportation guidelines can be applied in lieu of special requirements on privately controlled sites where conditions and requirements of use are similar to public thoroughfares.

8.3.2 Noncommercial Equipment and Special Operations

Special equipment used for the transport of hydrogen shall meet federal and state labor requirements (29 CFR) as well as additional requirements of the AHJ.

8.3.3 Guidelines for the Design of Noncommercial Transport Equipment

8.3.3.1 General Guidelines

When applicable, standard hydrogen design practice must be used (see Sections 3, 4, and 5) such as the following:

- The vessel design will be in accordance with accepted design practice (ASME BPVC; 49 CFR 178.338).
- Redundant relief protection must be provided to the vessel and piping systems.
- The process piping should be protected from collision damage by undercarriage, hampers, or other structure. Process piping should be designed to be empty during transportation and shear downstream of the vessel isolation valve in the event of an accident.
- The vessel must be insulated such that the holding time is sufficient to prevent hydrogen venting while the vehicle is in motion.
- The trailer shall use a fail-safe emergency brake system.

8.3.3.2 Requirements for Highway Service

The design of noncommercial vehicles must comply with federal and state transportation guidelines (Section 8.2) for operation on public thoroughfares. Any cargo tank must meet highway standards for cargo tank design (49 CFR 178.338 for cryogenic transport; 49 CFR 178.337 for gas carriers).

8.3.4 General Operating Procedures

The following guidelines apply to all hydrogen operations.

8.3.4.1 General

Areas shall be clear of nonessential personnel. Appropriate personnel protective equipment should be used. Maintenance of the necessary deluge systems shall be verified. All equipment including transport system, transfer equipment, and facility shall be grounded.

It shall be verified that no flame-producing devices are located within the operational area. Spark-producing and electrical equipment within the operational area and not hazard-proof shall be turned off and locked out. All tools used shall comply with established safety requirements. All vessel inlets and outlets, except safety relief devices, shall be marked to designate whether they are covered by vapor or liquid when the vessel is filled.

Transport containers shall be located over noncombustible surfaces when in operation.

It is the intent of DOT code that the extinguisher be used on small fires (engine, brakes, tires, etc.) originating from the trailer or transport equipment, not the hydrogen storing vessel. It shall be verified that trailers are equipped with a dry-chemical fire extinguisher. The rating shall not be less than 10 BC.^{‡‡}

Transfer must be stopped, and the leak must be repaired in the event of a hydrogen leak. Hydrogen sources should be isolated as quickly as possible in the event of a hydrogen fire.

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^{‡‡} Numerical rating pertains to the square footage of coverage by the extinguisher and the letter designation gives the fire classification (B=Flammable Liquids, C=Energized Equipment), see the NFPA 10 Standard for Portable Fire Extinguishers.

The atmosphere shall be sampled for safe hydrogen limits (less than 25% of the LFL) before motor vehicles are permitted to operate within the control area.

Operational procedural checklists shall be used.

8.3.4.2 Repair Operations

The system shall be verified safe according to procedures described in Section 7.1.5 before any type of maintenance is attempted.

Repairs, alterations, cleaning, or other operations performed in confined spaces in which hydrogen vapors or gases are likely to exist shall be in accordance with Section 7.1.4. The personnel engaged in the operations shall be advised of the hazards that may be encountered, and an attendant shall be immediately available while the work is being performed to administer emergency rescue if necessary.

8.3.4.3 Venting Operations

Facility venting should be used when possible.

A safe location in the field, remote if possible, should be selected for venting. Consideration should be given to the wind direction so vented gas will be safely carried away.

Boil-off gases from LH₂ can ignite in the cargo tank vent stack. Fire suppression should involve shutting off the hydrogen flow, when possible, by closing the vent valve. Helium, if available, can be applied to the vent stack discharge. The vent valve can be opened after the fire is out and the vent stack has cooled.

8.3.5 Inspection, Certification, and Recertification of Mobile Vessels

Testing and certification of mobile vessels for GH₂ and for LH₂ shall be in accordance with 49 CFR 178.337 and 49 CFR 178.338, respectively. Recertification for mobile vessels shall be in accordance with 49 CFR 180.407.

8.4 Transportation Emergencies

8.4.1 Initial Actions

The first concern in the event of a transportation emergency shall be to prevent death or injury. Try to get the dewar off the road, if possible, preferably to an open location if an accident or emergency occurs. Shut-off the tractor-trailer electrical system. Post warning lights and signs and keep people at least 152 m (500 ft) away. Contact authorities and obtain help by calling the following:

- 1) On site: call the number designated by the AHJ
- 2) Off site: call CHEMTREC at 1-800-424-9300 (current as of the time of publication, but subject to change)

8.4.2 Emergency Actions

Emergency actions to combat leaks and fires involving hydrogen tractor-trailers include pulling the vehicle into the least hazardous area and turning the ignition off. Emergency actions for which the driver is responsible include minor fires with the transport system (engine, brakes, tires, etc.) and vent system, which if left to escalate may lead to a severe hazard. Releases that involve the hydrogen storage system should be handled with extreme caution and/or evacuation of the vehicle and immediate area. Parking the leaking tractor-trailer in an open area limits the possibility of partial confinement and decreases the chance of significant pressure rises should the mixture ignite. A fire extinguisher should be used for fires originating near the engine; water or chemical fire extinguishers should be used for tire fires. Tires may reignite 20 to 30 min after the initial fire has been extinguished; therefore, the driver should not leave the scene until the tire temperature is sufficiently lowered. The driver also should not leave the scene until the fire has been completely extinguished and the burning materials cooled. Aid should be requested from

the nearest fire or police department. On the highway, the environment in which a fire and subsequent damage may occur is difficult to control. An accident may occur at any time and place along the route. A controlled release of hydrogen from the trailer through venting should take into account all possible ignition sources, vapor dispersion, population exposure, and general safe operations. Flares normally used for highway vehicular accident identification should not be used in close proximity to upset or damaged LH_2 vessels.



9 Emergency Procedures

9.1 General

9.1.1 Emergency Action Plan

An emergency action plan shall be developed and implemented. The emergency action plan shall be in writing and shall cover those designated actions employers and employees must take to ensure employee safety from fire and other emergencies (29 CFR 1910.38).

9.1.1.1 General Elements

The following elements, at a minimum, shall be included in the plan (29 CFR 1910.38):

- Emergency escape procedures and emergency escape route assignments
- Procedures to be followed by employees who remain to operate critical plant operations before they
 evacuate
- Procedures to account for all employees after emergency evacuation have been completed
- Rescue and medical duties for those employees who are to perform them
- The preferred means of reporting fires and other emergencies
- Names and regular job titles of persons for further information or explanation of duties under the plan

9.1.1.2 Other Elements

Other elements that emergency plans should include are procedures for the following situations:

- Actions by initially responding personnel (the initial responders should be identified in the emergency plans)
- Appropriate fire suppression response
- Establishment and maintenance of communications
- Appropriate medical response
- · Summoning outside assistance
- Establishing security
- Possible media coverage
- Salvage and restoration operations
- Establishing a command post with a predesignated line of authority
- Hazardous material inventory (29 CFR 1910.120)
- Situations involving asbestos

9.1.2 Alarm System

The AHJ shall establish an employee alarm system (29 CFR 1910.165). A distinctive signal for each purpose shall be used if the employee alarm system is used for alerting fire brigade members or for other purposes (29 CFR 1910.38).

9.1.3 Incident Management System

The AHJ shall adopt and implement an incident management system (IMS) in accordance with NFPA 1561. The IMS shall be used when managing a disaster or emergency.

9.1.4 Incident Command System

The senior emergency response official responding to an emergency shall become the individual in charge of a site specific incident command system (ICS). All emergency responders and their communications shall be coordinated and controlled through the individual in charge of the ICS assisted by the senior official present for each employer (29 CFR 1910.120).

9.1.5 Training

The AHJ shall designate and train a sufficient number of persons to assist in the safe and orderly emergency evacuation of employees before implementing the emergency action plan. The AHJ shall review the plan at the following times (29 CFR 1910.38):

- During initial plan development
- During changes in employee responsibilities or designated actions under the plan
- During plan changes

9.2 Types of Emergencies

9.2.1 General

The principal danger from a leak or spill is the potential for cryogenic burns and fires. Ventilation of storage, transfer, and use areas and the avoidance of ignition sources helps reduce the danger of fire.

Trucks, automobiles, or tank cars shall not be allowed through the area when spills occur, until the AHJ has certified the area to be safe for operations. The area shall be completely roped off and signs shall be posted. A person shall be stationed in a safe location upwind to warn others of danger if rope or signs are not available.

The source of supply shall be immediately shut off when a liquid leak or spill occurs in the piping from a vessel or a pumping system. The system can be disassembled and the leak can be repaired after the equipment or piping has been thoroughly vented and purged.

Catastrophic fires can be prevented by training personnel in their duties. It is important to remember that if the fire is extinguished without stopping the gas flow, an explosive mixture may form, making a more serious hazard than the fire itself. The approach generally should be to prevent the fire from spreading and let it burn until the hydrogen is consumed.

High-pressure GH leaks are more frequently heard than seen. Operations shall be immediately stopped, the supply source shall be isolated from the leaking system, and the line (or the system) shall be relieved of any pressure as soon as leaks are noted. Operations shall resume only after the repairs are completed.

9.2.2 Controllable Leaks

Controllable leaks are relatively small leaks that would not result in significant spill quantity before block, shut-off, and relief valves can be made operational. The AHJ is responsible for establishing procedures for small GH₂ leaks when such leaks have been shown to present no hazard to personnel, equipment, or facilities.

9.2.3 Uncontrollable Leaks

Uncontrollable leaks may be large and involve major spills. Actions to be taken shall be directed to the safety of personnel. Procedures to be followed include the following:

- The supply source shall be shut off if possible.
- The area shall be evacuated to 152 m (500 ft) from the spill source.
- Safety and fire departments shall be notified.
- Adjacent equipment shall be cooled down in case of fire.

9.2.4 Handling Gas Leaks from Cylinders

Only an acceptable, approved leak-detection solution shall be used when testing for leaks.

If a cylinder safety device leaks, personnel shall not attempt to correct the leak by tightening the safety device cap while the cylinder is under pressure. The contents of the cylinder shall be emptied in a safe location. The cap shall be removed to examine the condition of the threads, correct the damage, and pressurize and test for leaks.

Leaking commercial cylinders should be safely vented, tagged as defective, and returned to the supplier.

9.2.5 Handling Cylinder Fires

Personnel shall not try to put a fire out unless the cylinder is in the open or in a well-ventilated area free of combustibles and ignition sources. Extreme care should be taken in attempting to extinguish the fire. The process may create a mixture of air and escaping hydrogen that, if reignited, might explode.

In most instances, personnel shall not attempt to remove the burning cylinder, but the burning cylinder and any surrounding cylinders and combustibles should be kept cool by spraying them with water.

The hazard presented by the possibility of the flame increasing in size and intensity, and the possibility of igniting other cylinders or combustibles, shall be kept in mind when making the decision to move a burning cylinder.

When a group of cylinders is burning, it is extremely important that the persons fighting the fire do so from as great a distance as practicable. Personnel should be protected against the possibility of fragments or shrapnel should an explosion occur. The efforts of fire fighters in such instances should be directed toward keeping the cylinders cool and preventing adjacent equipment and buildings from catching fire.

9.2.6 Hydrogen Spills

Experiments on the dispersion of flammable clouds resulting from LH_2 spills have been conducted. Such data are necessary for evaluating the safety of hydrogen systems and separation distances from buildings and roadways and developing satisfactory ignition and spill controls. Although tests with SLH_2 have not been conducted, the data from the tests should apply to SLH_2 systems, except for the additional energy required to melt the solid particles.

Table A4.1 summarizes data obtained in experiments performed by A. D. Little, Inc. (1961) and by Zebetakis and Burgess (1961). Gas evolution rates measured with a gas meter were compared with calculated vaporization rates. Most of the A. D. Little, Inc. (1961) vaporization data were obtained from tests in a 0.6-m (2-ft) diameter, vacuum-insulated cylinder. Data for spills on sand and bank gravel exhibited an initial vaporization rate of 2.12 mm/s to 2.96 mm/s (5 in./min to 7 in./min), decreasing to an apparently constant liquid regression rate of about 0.635 mm/s (1.5 in./min).

Experiments (Witcofsky and Chirivella 1982) provide basic information regarding the physical phenomena governing the dispersion of flammable clouds resulting from large LH₂ spills. The experiments consisted

of ground spills of LH_2 as large as $5.7\,\mathrm{m}^3$ (1,500 gal), with spill durations of approximately 35 s. Instrumented towers downwind of the spill site gathered data on the temperature, hydrogen concentration, and turbulence levels as the hydrogen vapor cloud drifted downwind. Visual phenomena were recorded by motion picture and still cameras. Results of the experiments indicate, for rapid spills, thermal and momentum-induced turbulences cause the cloud to disperse to safe concentration levels and to become positively buoyant long before mixing from normal atmospheric turbulence becomes a major factor. On the basis of the LH_2 spill quantities, rates, and modes reported and the limited data analyses conducted, the following conclusions were drawn:

- Rapid LH₂ spills that might occur from a storage facility rupture are characterized by a brief period of ground-level flammable cloud travel during which the violent turbulence generated by the momentum of the spill, the quick phase change from a liquid to a vapor, and the thermal instability of the cloud cause the hydrogen vapors to mix quickly with air, disperse to nonflammable concentrations, warm up, and become positively buoyant. The ground-level cloud travels approximately 50 to 100 m (164 to 328 ft) and then rises at 0.5 to 1.0 m/s (1.64 to 3.28 ft/s).
- Prolonged, gentle spills or spills that might occur from an LH₂ pipeline rupture are characterized by prolonged ground-level cloud travel. Ground-level cloud travel is prolonged by low spill or momentuminduced cloud turbulence and suspected to be aggravated by long-term ground cooling (the major heat transfer mechanism for determining the vaporization rate).
- The use of dikes around LH₂ storage facilities probably prolongs ground-level flammable cloud travel. It may be preferable not to use dikes and take advantage of the dispersion mechanisms provided by spill and vaporization-induced turbulence.

9.3 Assistance in Emergencies

Responsible safety personnel shall monitor operations to ensure all safety precautions are taken during transfer, loading, testing, and disposal operations. Assistance in any emergency shall be available from those knowledgeable of safety and trained to deal with such an emergency.

9.3.1 Fire and Police Departments

Fire department personnel shall be informed of operations to be undertaken and when they will begin. Fire department assistance in an emergency shall be under the direction of the senior fire-fighting officer.

Fire fighters and police who respond to a spill, fire, or vehicle collision should be familiar with the hazard information cards recommended by the DOT or other safety documents (NASA Handbook (NHB) 2710.1). They should also know the recommended exclusion areas to protect the public if a spill or fire occurs. An additional factor for increased safety is awareness of fragment evacuation distance criteria. Guidance should be provided to limit danger from fragments and reduce the probability of injuries or fatalities in explosions.

9.3.2 Site Personnel

Site personnel, trained in handling specific mishaps and accidents, may be assigned definite tasks to perform in an emergency. These tasks shall be assigned by the AHJ.

9.3.3 Security

Security personnel shall be informed of actions to be undertaken and prepared to assist in an emergency.

9.4 Fire Suppression

9.4.1 General

The only positive way of handling a hydrogen fire is to let it burn under control until the hydrogen flow can be stopped. A hazardous combustible mixture starts forming at once if the hydrogen fire is extinguished

and the hydrogen flow is not stopped. It is very possible that the mixture will ignite with an explosion to cause more damage and restart the fire.

Although the hydrogen fire should not be extinguished until the hydrogen flow can be stopped, water sprays, etc., shall be used to extinguish any secondary fire and prevent the spread of the fire. The hydrogen-containing equipment should be kept cool by water sprays to decrease the rate of hydrogen leakage and prevent further heat damage.

There may be critical areas within or near a hydrogen facility where the occurrence of a fire or other related mishap demands a unique response from workers in the area, the safety organization, the security or police force, and responding fire fighters or emergency medical technicians. Existing routine procedures may not reflect the occurrence of such events or prove useful in structuring an effective response. Comprehensive planning for response to emergency situations shall be undertaken after a thorough analysis of the potential hazards. See 29 CFR 1910.38, 29 CFR 1910.120, and 29 CFR 1910.156.

Fire extinguishing equipment meeting the requirements of 29 CFR 1910.120 shall be on hand for ready use to control incipient fires.

Section 4.9 describes the design and installation of fixed fire suppression systems.

Employees, other than trained professional firefighters, trained volunteers, or emergency response personnel, shall not fight fires except in cases in which the fire is incipient in nature.

Carbon dioxide may be used in the presence of hydrogen fires. Although some toxic carbon monoxide may be produced in the flame, it will not be a large amount. Anyone breathing in the hot flame gases will be affected regardless of the presence of carbon monoxide. The carbon monoxide will be reduced to tolerable levels by the time the flame gases are diluted with fresh air and reach breathable temperatures. Confined spaces shall be well-ventilated and verified as safe as described in Section 4.4.5 before they are entered, unless the appropriate protective apparatuses are being used. Dry chemicals are better than carbon dioxide because they make the flames visible.

Remotely-controlled water-spray equipment, if it has been installed, should be used instead of hoses to cool equipment and reduce the spread of fire. If it is necessary to use hoses, personnel using them shall stay behind protective structures.

9.4.2 Actions against GH₂ Fires

Actions against GH₂ fires shall be in accordance with emergency action plans, including supervision as directed by the ICS.

The GH₂ supply shall be isolated if possible. Hydrogen systems shall be designed to stop the gas flow in an emergency.

Fog and solid-stream nozzles are the most adaptable in controlling fires. Dry-chemical extinguishers, carbon dioxide, nitrogen, and steam extinguish small hydrogen fires. Water shall be sprayed on adjacent equipment to cool it as necessary.

9.4.3 Actions against LH₂ Fires

Actions against LH₂ fires shall be in accordance with emergency action plans, including supervision as directed by the ICS.

The LH_2 supply shall be isolated if possible. Hydrogen systems shall be designed to stop the liquid flow in an emergency. Care shall be taken to prevent spraying water on or into vent openings when using water to suppress LH_2 fires (NFPA 50B). Water shall not be applied if the inner surface is exposed. The only action in case of ignition of a massive LH_2 spill is to keep adjacent equipment and facilities cool by spraying them with water.

9.5 First-Aid for Cryogenic-Induced Injuries

9.5.1 Procedures

The procedures for cold injuries provided in this section were the most current available at the time of the preparation of this Guide. These procedures may change, and anyone dealing with cryogenic hydrogen systems should keep informed on the latest recommended procedures.

Direct physical contact with LH₂, cold vapor, or cold equipment can cause serious tissue damage. Medical assistance should be obtained as soon as possible for any cold injury. First aid procedures to be administered by medical professionals are beyond the scope of this Guide. However, proper immediate bystander response should be as follows:

- If it is safe to do so, remove the patient from the source of the cold.
- In the event of limb-size or smaller cryogenic exposure, appropriate response may include an attempt to rapidly warm the affected area with moist heat from a shower, eyewash, or warm water bath (not to exceed 38.9 °C (102 °F)). However, do not allow a heavy stream of water to impinge on frozen skin. In some cases, it is safest to do nothing other than cover the involved area until professional medical help is available.
- Massive full-body cryogenic exposures present significant additional concerns, but removal of the
 victim from the exposure atmosphere and keeping the victim's airway open are important. Loosely
 wrapping the victim in a blanket until the arrival of the ambulance team is also advised.
- Some important don'ts:
 - Don't remove frozen gloves, shoes, or clothing. Salvageable skin may be pulled off inadvertently.
 - Don't massage the affected part.
 - **Don't** expose the affected part to temperatures higher than 44 °C (112 °F), such as a heater or a fire. This superimposes a burn and further damages already injured tissues.
 - **Don't** apply snow or ice.
 - Don't apply ointments.
 - Don't allow any smoking, open flames, or other hazardous conditions near the victim.

9.5.2 Training

Education of the risk of cold injury as well as preventive and emergency care must be incorporated into training programs for operations and emergency response.

9.6 Safeguards for Entering Permit-Required Confined Spaces

Personnel entering a confined space that may be subject to oxygen enrichment, oxygen depletion, toxic chemicals, or hydrogen gas shall follow approved practices and procedures (29 CFR 1910.146 1996).

Acceptable entry conditions that must exist in a permit space to allow entry are as follows:

- Oxygen content shall be between 19.5% and 23.5% by volume, otherwise an appropriate breathing apparatus shall be used.
- Hydrogen content shall be less than 10% of LFL (less than 0.4% by volume).
- Atmospheric concentrations of any substance that may expose personnel to risk of death, incapacitation, impairment of ability to self-rescue, injury, or acute illness shall be below the limits established in 29 CFR.

Personnel entering permit-required confined spaces shall have an attendant present and area life-line or other approved safety removal equipment as required.

The internal atmosphere shall be tested, before personnel enter permit-required confined spaces, with a calibrated direct reading instrument for the following conditions in the order given:

- Oxygen content
- Flammable GH₂ gases and vapors
- Potential toxic air contaminants



Annex A Figures and Tables (Informative)

A.1 Hydrogen Chemical and Physical Properties

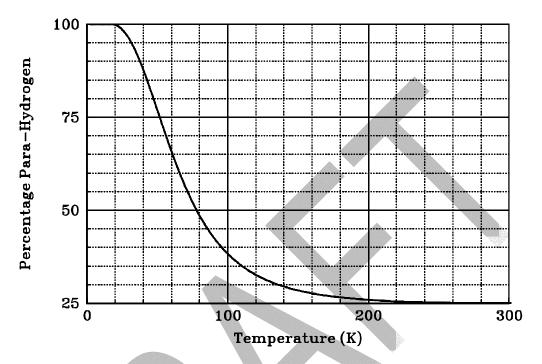


Figure A1.1 — Equilibrium percentage of para-hydrogen vs. temperature (McCarty et al. 1981)

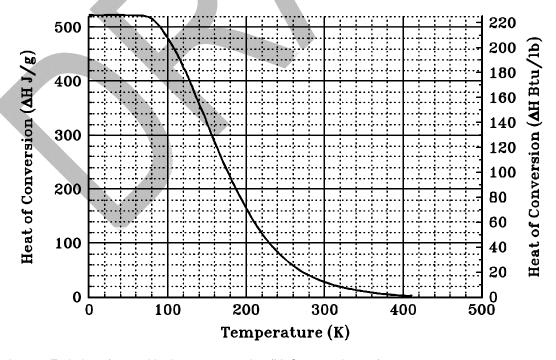


Figure A1.2 — Enthalpy of normal hydrogen conversion (McCarty et al. 1981)

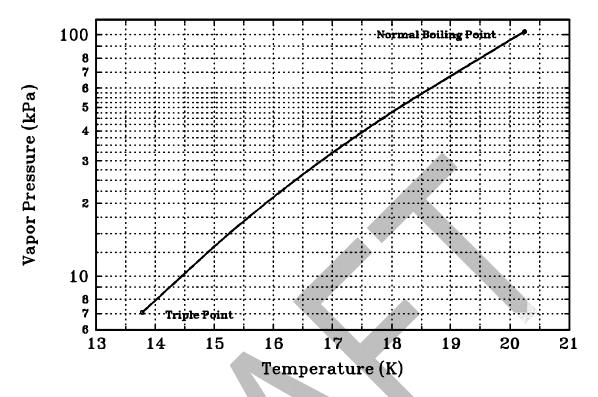


Figure A1.3 — Vapor pressure of liquefied para-hydrogen from the triple point to the NBP (McCarty et al. 1981)

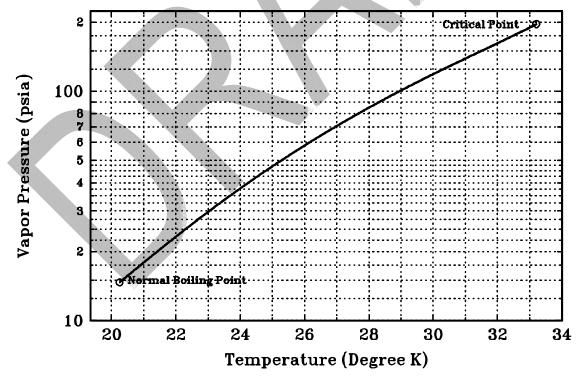


Figure A1.4 — Vapor pressure of LH₂ from the NBP to critical point (McCarty et al. 1981)

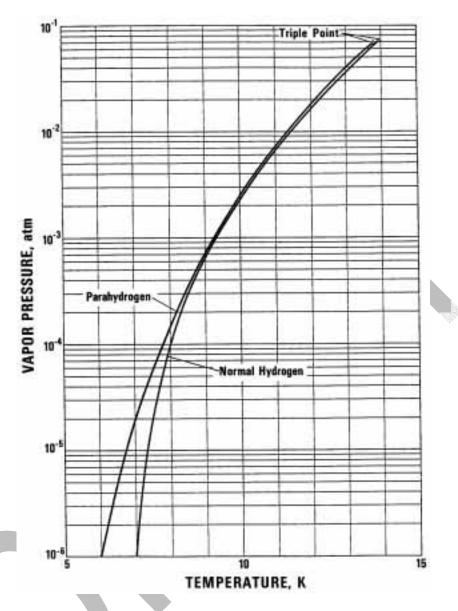


Figure A1.5 — Vapor pressure of normal and para-hydrogen below the triple point (McCarty et al. 1981)

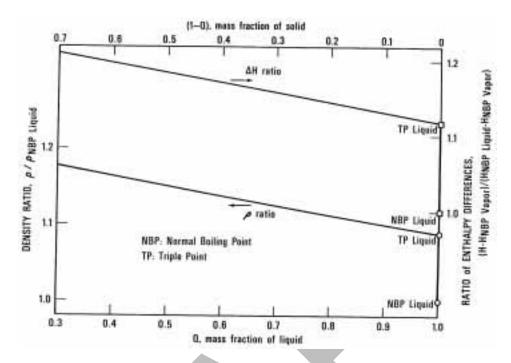


Figure A1.6 — Comparison of density and bulk fluid heat capacity for slush, triple-point liquid, and NBP liquid parahydrogen (McCarty et al. 1981)

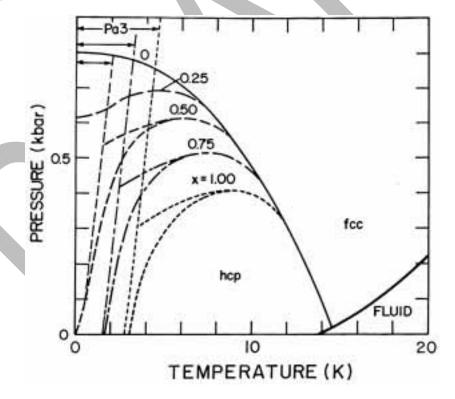


Figure A1.7 — Proposed phase diagram (P-T plane) for solid hydrogen at various ortho-hydrogen mole fractions, x. Alternate branches are shown for hexagon close packed (hcp)-face centered cubic (fcc) transition. Heavy solid line is melting curve (McCarty et al. 1981).

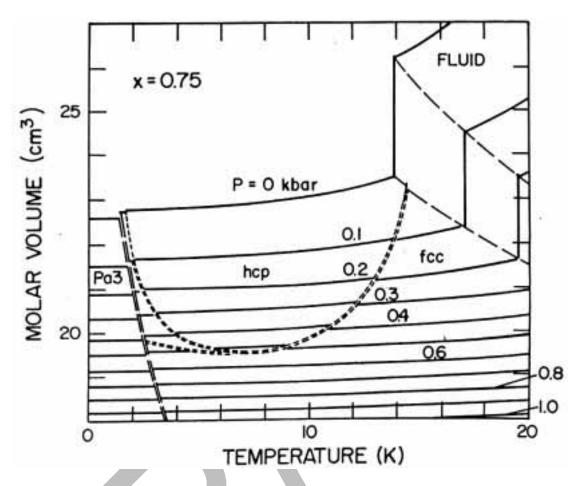


Figure A1.8 — Proposed phase diagram (V-T plane) for solid normal hydrogen. Dashed lines indicate alternate branches for hexagonal close packed (hcp)-face centered cubic (fcc) transition curve. x = mole fraction (McCarty et al. 1981).

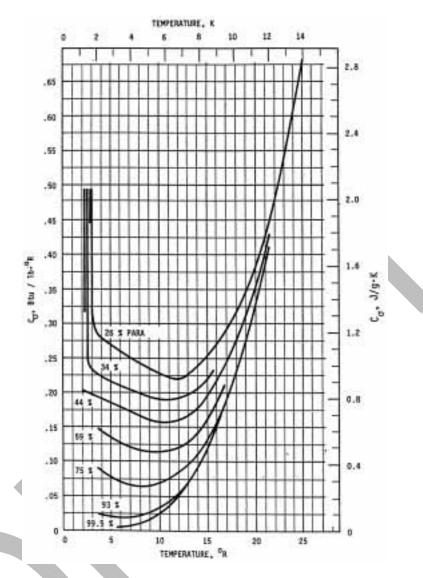


Figure A1.9 — Specific heat (heat capacity) of saturated solid hydrogen (McCarty et al. 1981)

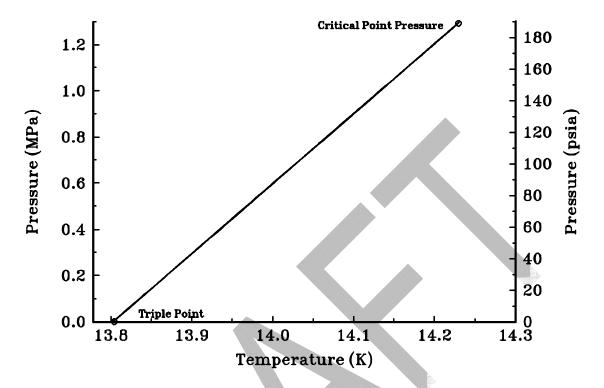


Figure A1.10 — Melting line from triple point to critical point pressure for para-hydrogen (McCarty et al. 1981)

Table A1.1 — Selected physical, thermophysical, chemical, and combustion properties of gaseous, liquefied, slush, and solid para-hydrogen^a

Normal temperature and pressure (NTP) $^{\circ}$ properties Density of GH ₂ 83.764 g/m ³ 0.00523 lb _m /ft ³ Density of air (for comparison) 1.198 g/m ³ 0.0749 lb _m /ft ³ Specific heat at constant pressure, C _p 14.89 kJ/kg·K 3.559 Btu/lb _m ·°R Specific heat ratio, $\gamma = C_{\nu}/C_{\nu}$ 1.383 Enthalpy 4,097.7 kJ/kg 1,762.8 Btu/lb _m Internal Energy 2,888.0 kJ/kg 1,242.5 Btu/lb _m Entropy 64.44 kJ/kg·K 15.40 Btu/lb _m °R Velocity of sound (adiabatic) 1,294 m/s 4,246 ft/s Viscosity 8.81 μPa·s 0.00881 centipoise Thermal conductivity, k 191.4 mW/m·K 0.111 Btu/ft·h·°R Dielectric constant, ε 1.00026 Compressibility factor, Z 1.0006 Index of refraction 1.00012 Critical point properties 1,292.8 kPa abs 187.5 psia Density 31.43 kg/m ³ 1.96 lb _m /ft ³ Specific heat at saturation, C _σ (very large) Specific heat at constant pressure, C _p (very large) Specific heat ratio, $\gamma = C_{\nu}/C_{\nu}$ (large) Enthalpy 17.6 kJ/kg·K 4.20 Btu/lb _m 1.22 Btu/lb _m Internal Energy 2.83 kJ/kg 1.22 Btu/lb _m Internal Energy 2.83 kJ/kg 1.22 Btu/lb _m Velocity of sound 350 m/s 1148 ft/s Normal Boiling Temperature Normal boiling point (NBP) properties Normal Boiling Temperature 1.098 Normal Boiling Temperature Normal boiling point (NBP) properties Normal Boiling Temperature Normal boiling point (NBP) properties Normal Boiling Temperature Normal Boiling Temperature Normal boiling point (NBP) properties Normal Boiling Temperature Normal boiling point (NBP) properties Normal Boiling Temperature Norm	and solid para-hydrogen ^a		
Density of GH ₂	Molecular Weight	2.01594	
Density of air (for comparison)			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			
Specific heat ratio, $\gamma = C_p/C_v$ 1.383 Enthalpy 4.097.7 kJ/kg 1.762.8 Btu/lb _m Internal Energy 2.288.0 kJ/kg 1.242.5 Btu/lb _m Entropy 64.44 kJ/kg·K 15.40 Btu/lb _m °R Velocity of sound (adiabatic) 1,294 m/s 4,246 ft/s Viscosity 8.81 µPa·s 0.00881 centipoise Thermal conductivity, k 191.4 mW/m·K 0,111 Btu/ft·h·°R Dielectric constant, ε 1.00026 Compressibility factor, Z 1.0006 Index of refraction Critical point properties Temperature 32.976 K 7-Pressure 1,292.8 kPa abs 187.5 psia Density 31.43 kg/m³ 1.96 lb _m /ft³ Specific heat at saturation, C_{σ} (very large) Specific heat at constant pressure, C_p Specific heat at constant pressure, C_p (large) Enthalpy 38.49 kJ/kg 16.56 Btu/lb _m Internal Energy 2.83 kJ/kg 1.22 Btu/lb _m Entropy 47.6 kJ/kg·K 4.20 Btu/lb _m FR Velocity of sound 350 m/s 1148 ft/s Viscosity Dielectric constant, ε 1.098 Compressibility factor, Z 0.085 lb _m /ft³ Pressure 1.028 k 4.23.2 °F Pressure 1.038 kg/m³ 0.0835 lb _m /ft³			
Enthalpy	Specific heat at constant pressure, Cp	14.89 kJ/kg·K	3.559 Btu/lb _m ⋅°R
Enthalpy	Specific heat ratio, $\gamma = C_p/C_v$	1.383	
		4,097.7 kJ/kg	1,762.8 Btu/lb _m
	Internal Energy	2,888.0 kJ/kg	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Entropy	64.44 kJ/kg·K	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Velocity of sound (adiabatic)	1,294 m/s	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Thermal conductivity, k	191.4 mW/m·K	0.111 Btu/ft·h·°R
$ \begin{array}{ c c c c }\hline & & & & & & & & & & & & & & & & & \\ \hline \textbf{Temperature} & & & & & & & & & & & & & & & & & & &$	Dielectric constant, ε	1.00026	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			
Temperature 32.976 K $-400.6 ^{\circ}\text{F}$ Pressure $1,292.8 \text{kPa}$ abs 187.5psia Density 31.43kg/m^3 $1.96 \text{lb}_m / \text{ft}^3$ Specific heat at saturation, C_{σ} (very large)Specific heat at constant pressure, C_p (very large)Specific heat ratio, $\gamma = C_p / C_v$ (large)Enthalpy 38.49kJ/kg 16.56Btu/lb_m Internal Energy 2.83kJ/kg 1.22Btu/lb_m Entropy 17.6kJ/kg·K $4.20 \text{Btu/lb}_m \cdot ^{\circ}\text{R}$ Velocity of sound 350m/s 1148ft/s Viscosity $3.5 \mu \text{Pa·s}$ 0.0035centipoise Thermal conductivity, k(anomalously large)Dielectric constant, ε $1.098 \text{Compressibility factor, Z}$ Normal boiling point (NBP) propertiesNormal Boiling Temperature (NBT) 20.268K $-423.2 ^{\circ}\text{F}$ Pressure 101.3kPa 14.696psia Density 1.338kg/m^3 $0.0835 \text{lb}_m / \text{ft}^3$			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Critical	point properties	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Temperature		-400.6 °F
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			187.5 psia
Specific heat at constant pressure, C_p (very large) Specific heat ratio, $\gamma = C_p/C_v$ (large) Enthalpy 38.49 kJ/kg 16.56 Btu/lbm Internal Energy 2.83 kJ/kg 1.22 Btu/lbm Entropy 17.6 kJ/kg·K 4.20 Btu/lbm·°R Velocity of sound 350 m/s 1148 ft/s Viscosity 3.5 μ Pa·s 0.0035 centipoise Thermal conductivity, k (anomalously large) Dielectric constant, ϵ 1.098 Compressibility factor, Z 0.3025 Normal Boiling Temperature (NBT) 20.268 K -423.2 °F Pressure 101.3 kPa 14.696 psia Density of vapor 1.338 kg/m³ 0.0835 lbm/ft³			1.96 lb _m /ft ³
Specific heat ratio, $\gamma = C_p/C_v$ (large) Enthalpy 38.49 kJ/kg 16.56 Btu/lb _m Internal Energy 2.83 kJ/kg 1.22 Btu/lb _m Entropy 17.6 kJ/kg·K 4.20 Btu/lb _m ·°R Velocity of sound 350 m/s 1148 ft/s Viscosity 3.5 µPa·s 0.0035 centipoise Thermal conductivity, k (anomalously large) Dielectric constant, ε 1.098 Compressibility factor, Z 0.3025 Normal Boiling Temperature (NBT) 20.268 K -423.2 °F Pressure 101.3 kPa 14.696 psia Density of vapor 1.338 kg/m³ 0.0835 lb _m /ft³	Specific heat at saturation, C _σ	(very large)	
Enthalpy 38.49 kJ/kg 16.56 Btu/lbm Internal Energy 2.83 kJ/kg 1.22 Btu/lbm Entropy 17.6 kJ/kg·K 4.20 Btu/lbm·°R Velocity of sound 350 m/s 1148 ft/s Viscosity 3.5 μPa·s 0.0035 centipoise Thermal conductivity, k (anomalously large) Dielectric constant, ε 1.098 Compressibility factor, Z 0.3025 Normal boiling point (NBP) properties Normal Boiling Temperature (NBT) 20.268 K -423.2 °F Pressure 101.3 kPa 14.696 psia Density O.0835 lbm/ft³	Specific heat at constant pressure, Cp	(very large)	
Internal Energy 2.83 kJ/kg 1.22 Btu/lbm	Specific heat ratio, $\gamma = C_p/C_v$	(large)	
Entropy 17.6 kJ/kg⋅K 4.20 Btu/lbm⋅ °R Velocity of sound 350 m/s 1148 ft/s Viscosity 3.5 μPa⋅s 0.0035 centipoise Thermal conductivity, k (anomalously large) Dielectric constant, ε 1.098 Compressibility factor, Z 0.3025 Normal boiling point (NBP) properties Normal Boiling Temperature (NBT) 20.268 K -423.2 °F Pressure 101.3 kPa 14.696 psia Density 1.338 kg/m³ 0.0835 lbm/ft³	Enthalpy	38.49 kJ/kg	16.56 Btu/lb _m
Velocity of sound350 m/s1148 ft/sViscosity3.5 μPa·s0.0035 centipoiseThermal conductivity, k(anomalously large)Dielectric constant, ε1.098Compressibility factor, Z0.3025Normal boiling point (NBP) propertiesNormal Boiling Temperature (NBT)20.268 K-423.2 °FPressure101.3 kPa14.696 psiaDensity1.338 kg/m³0.0835 lbm/ft³	Internal Energy	2.83 kJ/kg	1.22 Btu/lb _m
Velocity of sound350 m/s1148 ft/sViscosity3.5 μPa·s0.0035 centipoiseThermal conductivity, k(anomalously large)Dielectric constant, ε1.098Compressibility factor, Z0.3025Normal boiling point (NBP) propertiesNormal Boiling Temperature (NBT)20.268 K-423.2 °FPressure101.3 kPa14.696 psiaDensity1.338 kg/m³0.0835 lbm/ft³	Entropy	17.6 kJ/kg·K	4.20 Btu/lbຼ·°R
Viscosity Thermal conductivity, k Dielectric constant, ε Compressibility factor, Z Normal boiling point (NBP) properties Normal Boiling Temperature (NBT) Pressure 1.338 kg/m³ 0.0035 centipoise 0.0035 centipoise 0.0035 centipoise 0.0035 centipoise 0.0035 centipoise 1.098 1.098 1.098 1.098 1.098 1.098 1.098 1.098 1.098 1.0035 centipoise 1.098	Velocity of sound	350 m/s	1148 ft/s
Dielectric constant, ε 1.098 Compressibility factor, Z Normal boiling point (NBP) properties Normal Boiling Temperature (NBT) 20.268 K -423.2 °F Pressure 101.3 kPa 14.696 psia Density 1.338 kg/m³ 0.0835 lbm/ft³	Viscosity	3.5 µPa⋅s	0.0035 centipoise
Compressibility factor, Z Normal boiling point (NBP) properties Normal Boiling Temperature (NBT) 20.268 K Pressure 101.3 kPa 14.696 psia Density of vapor 1.338 kg/m ³ 0.0835 lb _m /ft ³	Thermal conductivity, k	(anomalously large)	
Normal boiling point (NBP) properties Normal Boiling Temperature (NBT) 20.268 K -423.2 °F Pressure	Dielectric constant, ε	1.098	
Normal Boiling Temperature (NBT) 20.268 K -423.2 °F Pressure 101.3 kPa 14.696 psia Density 1.338 kg/m³ 0.0835 lb _m /ft³	Compressibility factor, Z	0.3025	
Pressure 101.3 kPa 14.696 psia Density 1.338 kg/m³ 0.0835 lb _m /ft³	Normal boiling	g point (NBP) properties	
Density of vapor 1.338 kg/m ³ 0.0835 lb _m /ft ³	Normal Boiling Temperature (NBT)	20.268 K	-423.2 °F
of vapor 1.338 kg/m ³ 0.0835 lb _m /ft ³	Pressure	101.3 kPa	14.696 psia
of vapor 1.338 kg/m ³ 0.0835 lb _m /ft ³	Density		
1 of liquid 170.78 kg/m ³ 14.42 lb./ft ³		1.338 kg/m ³	0.0835 lb _m /ft ³
	of liquid	70.78 kg/m ³	4.42 lb _m /ft ³
Heat of vaporization 445.6 kJ/kg 191.7 Btu/lb _m		445.6 kJ/kg	191.7 Btu/lb _m
Specific heat at saturation, C_{σ}	Specific heat at saturation, C_{σ}		
of vapor -16.51 kJ/kg·K -3.95 Btu/lb _m ·°R	of vapor	-16.51 kJ/kg·K	-3.95 Btu/lb _m ·°R
of liquid 9.38 kJ/kg⋅K 2.24 Btu/lb _m ⋅°R		9.38 kJ/kg·K	2.24 Btu/lb _m ⋅°R
Specific heat at constant pressure, C _p	Specific heat at constant pressure, Cp		
of vapor 12.15kJ/kg·K 2.904 Btu/lb _m ·°R	of vapor	12.15kJ/kg·K	2.904 Btu/lb _m ·°R
of liquid 9.688 kJ/kg·K 2.315 Btu/lb _m ·°R	of liquid	9.688 kJ/kg·K	2.315 Btu/lb _m ·°R
Specific heat ratio, $\gamma = C_p/C_v$	Specific heat ratio, $\gamma = C_p/C_v$		
of vapor 1.869		1.869	
of liquid 1.688	of liquid	1.688	
Enthalpy			
of vapor 189.3 kJ/kg 81.5 Btu/lb _m			
of liquid -256.3 kJ/kg -110.2 Btu/lb _m	of liquid	-256.3 kJ/kg	-110.2 Btu/lb _m

Table A1.1 — Selected physical, thermophysical, chemical, and combustion properties of gaseous, liquefied, slush, and solid para-hydrogen^{a, b} (continued)

and solid para-hydrogen ^{a, b} (continued)		
Internal energy	1	1
of vapor	113.6 kJ/kg	48.87 Btu/lb _m
of liquid	-257.7 kJ/kg	-110.9 Btu/lb _m
Entropy		
of vapor	29.97 kJ/kg·K	7.162 Btu/lb _m ·°R
of liquid	7.976 kJ/kg·K	1.906 Btu/lb _m ·°R
Velocity of sound (adiabatic)		
of vapor	355 m/s	1,165 ft/s
of liquid	1,093 m/s	3,586 ft/s
Viscosity		
of vapor	1.1 µPa⋅s	0.0011 centipoise
of liquid	13.2 µPa⋅s	0.0132 centipoise
Thermal conductivity, k		
of vapor	16.9 mW/m·K	0.00977 Btu/ft·h·°R
of liquid	99 mW/m·K	0.0572 Btu/ft⋅h⋅°R
Dielectric constant, ε		
of vapor	1.0040	
of liquid	1.230	
Compressibility factor, Z		
of vapor	0.9061	
of liquid	0.01712	
Surface tension of liquid	0.00193 N/m	1.1 x 10 ⁻⁵ lb _f /in
Index of refraction of liquid	1.110	·
Tripl	e point properties	
Temperature	13.803 K	-434.8 °F
Pressure	7.04 kPa abs	1.02 psia
Density		
of vapor	0.1258 kg/m ³	0.00784 lb _m /ft ³
of liquid	77.03 kg/m ³	4.81 lb _m /ft ³
of solid	86.50 kg/m ³	5.40 lb _m /ft ³
Heat of fusion	58.29 kJ/kg	25.08 Btu/lb _m
Heat of vaporization	449.17 kJ/kg	193.2Btu/lb _m
Heat of sublimation	507.39 kJ/kg	218.3 Btu/lb _m
Specific heat at saturation, Cσ	,	2 2 33 311
of vapor	-23.28 kJ/kg·K	-5.57 Btu/lb _m ⋅°R
of liquid	6.87 kJ/kg·K	1.64 Btu/lb _m ·°R
of solid	2.84 kJ/kg·K	0.679 Btu/lb _m ·°R
Specific heat at constant pressure, Cp	= 10 1 Northg 11	3.0.0 D.ts/.is/iii
of vapor	10.52 kJ/kg·K	2.513 Btu/lb _m ·°R
of liquid	6.513 kJ/kg·K	1.557 Btu/lb _m ·°R
Specific heat ratio, $\gamma = C_0/C_v$	0.515 kg/kg-K	1.337 Btd/lb _m - K
	1.602	1
of vapor	1.693	
of liquid	1.382	
Enthalpy	4.40.2 to 1/1000	CO 4 Dtv/lb
of vapor	140.3 kJ/kg	60.4 Btu/lb _m
of liquid	-308.9 kJ/kg	-132.9 Btu/lb _m
of solid	-367.2 kJ/kg	-158.0 Btu/lb _m
Internal energy	04 00 1: 1/1:	2C 24 Dt./lb
of vapor	84.23 kJ/kg	36.24 Btu/lb _m
of liquid	-309.0 kJ/kg	-132.9 Btu/lb _m
of solid	-367.3 kJ/kg	-158.0 Btu/lb _m

Table A1.1 — Selected physical, thermophysical, chemical, and combustion properties of gaseous, liquefied, slush, and solid para-hydrogen^{a, b} (continued)

and solid para-hydrogen (continued)		
Entropy of vapor	27 52 k I/ka K	9.067.Dtu/lb
of Vapor of liquid	37.52 kJ/kg·K 20.16 kJ/kg·K	8.967 Btu/lb _m ·°R
of liquid of solid	0.739 kJ/kg·K	1.186 Btu/lb _m ·°R 0.177 Btu/lb _m ·°R
Velocity of sound	0.739 kJ/kg-K	U.177 Bid/ID _m · K
	305 m/s	1,001 ft/s
of vapor of liquid	1,273 m/s	4,177 ft/s
Viscosity	1,273 111/8	4,177 108
	0.74 uDo o	0.00074 centinging
of vapor of liquid	0.74 µPa⋅s 26.0 µPa⋅s	0.00074 centipoise
	26.0 μΡα-ς	0.026 centipoise
Thermal conductivity, k	40.4 = 10/4/== 10	0.00747 Dt./ft b 0D
of vapor	12.4 mW/m·K	0.00717 Btu/ft·h·°R
of liquid	73 mW/m·K	0.0422 Btu/ft-h°R
of solid	900 mW/m-K	0.52 Btu/ft·h·°R
Dielectric constant, ε	1 1 22222	
of vapor	1.00038	
of liquid	1.252	
of solid	1.286	
Compressibility factor, Z	10,0050	
of vapor	0.9850	
of liquid	0.001606	1 11 /4 3
Density of slush (50% by mass solid)	81.50 kg/m ³	5.09 lb _m /ft ³
Density of slush (50% by volume solid)	81.77 kg/m ³	5.11 lb _m /ft ³
	er properties	
Equivalent vol solid @ TP/vol liquid @ NBT	0.8181	
Equivalent vol gas @ NTP/vol liquid @ NBT	845.1	1
Pressure required to maintain NBP liquid density	172 MPa	25,000 psi
in NTP GH ₂ (fixed volume, no venting)	110 00 1/	54 570 Dt. (II
Heat of combustion (low)	119.93 kJ/g	51,573 Btu/lb _m
Heat of combustion (high)	141.86 kJ/g	61,003 Btu/lb _m
Limits of flammability in NTP air	4.0 vol % to 75.0 vol %	
Limits of flammability in NTP oxygen	4.1 vol% to 94.0 vol%	
Limits of detonability in NTP air	18.3 vol% to 59.0 vol%	
Limits of detonability in NTP oxygen	15 vol% to 90 vol%	
Stoichiometric composition in air	29.53 vol%	18=
Minimum energy for ignition in air	0.017 mJ	1.6 x 10 ⁻⁸ Btu
Autoignition temperature	858 K	1,085 °F
Hot air-jet ignition temperature	943 K	1,238 °F
Flame temperature in air	2,318 K	3,713 °F
Thermal energy radiated from flame to	17% to 25%	
surroundings	005 / 1 005 /	1404: / / 400: /
Burning velocity in NTP air	265 cm/s to 325 cm/s	104 in/s to 128 in/s
Detonation velocity in NTP air	1.48 km/s to 2.15 km/s	4,856 ft/s to 7054 ft/s
Diffusion coefficient in NTP air	0.61 cm ² /s	0.095 in ² /s
Diffusion velocity in NTP air	<2.0 cm/s	<0.79 in/s
Buoyant velocity in NTP air	1.2 m/s to 9 m/s	3.9 ft/s to 30 ft/s
Maximum experimental safe gap	0.008 cm	0.003 in.
in NTP air	0.004	0.005
Quenching gap in NTP air	0.064 cm	0.025 in.
Detonation induction distance in NTP air	L/D ≈ 100	
Limiting oxygen index	5.0 vol%	

Table A1.1 — Selected physical, thermophysical, chemical, and combustion properties of gaseous, liquefied, slush, and solid para-hydrogen^{a, b} (continued)

and cond para mydrogen (continuou)		
Vaporization rate (steady state) of	2.5 cm/s to 5.0 cm/s	1 in/s to 2 in/s
liquid pool without burning		
Burning rates of spilled liquid pools	0.5 mm/s to 1.1 mm/s	0.02 in/s to 0.04 in/s
Energy of explosion (theoretical explosive yield)	≈24 (g TNT)/(g H ₂)	≈24 (lb _m TNT)/(lb _m H ₂)
	0.17 (g TNT)/(kJ H ₂)	4.0 x 10 ⁻⁴ (lb _m TNT)/(Btu H ₂)
	$2.02 \text{ (kg TNT)/m}^3 \text{ NTP GH}_2)$	0.126 lb _m TNT)/(ft ³ NTP GH ₂)
	1.71 (g TNT)/(cm ³ NBP LH ₂)	107.3(lb _m TNT)/(ft ³ NBP LH ₂)



McCarty et al. 1981
Temperature-dependent ortho-para changes continue to influence properties in the solid state. Several properties (such as specific heat, thermal conductivity, and thermal diffusivity) are highly sensitive to actual ortho-para composition.

NTP = 293 K (68 °F) and 101.325 kPa (14.696 psi absolute)

Table A1.2 — Fixed point properties of normal hydrogen^a

	Triple Point				oiling Point			
Properties	Solid	Liquid	Vapor	Liquid	Vapor	Critical Point	STP	NTP
Temperature ^b , °F (K)	-434.55	-434.55	-434.55	-422.97	-422.97	-399.93	32.000	68.000
, , ,	(13.957)	(13.957)	(13.957)	(20.390)	(20.390)	(33.190)	(273.15)	(293.15)
Pressure, inches Hg	2.147	2.147	2.147	30.19	30.19	391.9	30.19	30.19
(mm Hg)	(54.04)	(54.04)	(54.04)	(760.0)	(760.0)	(9865)	(760.0)	(760.0)
Density, lb/ft ³	5.409	4.817	8.099 x 10 ⁻³	4.427	83.05 x 10 ⁻³	1.879	5.609 x 10 ⁻³	5.225 x 10 ⁻³
(mol/cm ³)	(0.04301)	(0.03830)	(0.0644 x 10 ⁻³)	(0.0352)	(0.6604×10^{-3})	(0.01494)	(0.0446×10^{-3})	(0.04155 x 10 ⁻³)
Specific volume, ft ³ /lb	0.1849	0.2076	123.5	0.2259	12.05	0.5322	178.3	191.38
(cm ³ /mol)	(23.25)	(26.11)	(15.530)	(28.41)	(1514)	(66.93)	(22.420)	(24.070)
Compressibility factor,	c	0.001621	0.9635	0.01698	0.9051	0.3191	1.00042	1.00049
Z = PV/RT								
Heats of fusion and	24.99	194.4		191.9	A	0		
vaporization, Btu/lb (J/mol)	(117.1)	(911.3)	· ·	(899.1)				
Specific heat, Btu/lb-°R (J/g-K)								
At saturation, C _σ	0.6794	1.642	-5.565	2.242	-3.946	very large		
, -0	(2.842)	(6.870)	(-23.28)	(9.380)	(-16.51)			
At constant pressure, C _p		1.569	2.516	2.336	2.917	very large	3.390	3.425
		(6.563)	(10.526)	(9.772)	(12.20)	, ,	(14.18)	(14.33)
At constant volume, C _v		1.130	1.484	1.375	1.565	2.336	2.407	2.419
		(4.727)	(6.211)	(5.754)	(6.548)	(9.772)	(10.07)	(10.12)
Specific heat ratio, $\gamma = C_p/C_v$		1.388	1.695	1.698	1.863	large	1.408	1.416
Enthalpy, Btu/lb (J/mol)	68.63	93.62	288.1	117.0	308.9	248.4	1654	1776
	(321.6)	(438.7)	(1350)	(548.3)	(1447)	(1164)	(7749)	(8324)
Internal energy, Btu/lb (J/mol)	67.84	92.83	263.5	116.5	276.2		1169	1256
	(317.9)	(435.0)	(1235)	(545.7)	(1294)		(5477)	(5885)
Entropy, Btu/hr °R (J/mol · K)	2.41	3.40	11.1	4.14	9.36	6.47	16.5	16.8
	(20.3)	(28.7)	(93.6)	(34.92)	(78.94)	(54.57)	(139.6)	(141.6)
Velocity of sound, ft/s (m/s)		4206	1007	3612	1171		4088	4246
	4	(1282)	(307)	(1101)	(357)		(1246)	(1294)
Viscosity,		0.026	0.00074	0.0132	0.0011	0.0035	0.00839	0.00881
centipoise (μPa·s)	337	(26)	(0.74)	(13.2)	(1.1)	(3.5)	(8.39)	(8.81)
Thermal conductivity, k	0.52	0.042	0.0072	0.057	0.0098	anomalously	0.098	0.106
Btu/ft·h·°R (μW/m·K)	(90)	(7.3)	(1.24)	(9.9)	(1.69)	large	(17.40)	(18.38)
Prandtl number		2.34	0.630	1.30	0.798		0.682	0.688
Dielectric constant, ε	1.287	1.253	1.00039	1.231	1.0040	1.0937	1.000271	1.000253
Index of refraction	1.134	1.119	1.000196	1.1093	1.0020	1.0458	1.000136	1.000126
Surface tension,		0.0171 x 10 ⁻³		0.0111 x 10 ⁻³		0		
lb _f /in (N/m)		(3.00×10^{-3})		(1.94 x 10 ⁻³)				
Equivalent volume per	0.0404		540.0		50.00	0.057	700.0	0.47.4
volume of liquid at NBT	0.8184	0.9190	546.3	1.000	53.30	2.357	789.3	847.1

McCarty et al. 1981
 These temperatures are based on the IPTS-1968 temperature scale
 Dashes indicate not applicable

Table A1.3a — Thermodynamic properties of the hydrogen solid-vapor two phase region^{a, b}

10010	A1.5a		Solid phase									Vapor phase			
P ^c	Te	v ^f	D ^g	н ^h	s ⁱ	u ^j	, k	١	,,, m	V					
atm	K	V 3				_	C _{sat}	C _p '	ΔH _{sub}	cm ³ /mol	mol/L	J/mol	J/mol · K	J/mol	
		cm /mol	mol/L	J/mol	J/mol · K	J/mol · K	J/mol · K	J/mol · K	J/mol					0	
0.06950	13.8	23.30	42.911	-740.2	1.500	-740.4	5.634	5.640	1022.1	16030	.06238	281.9	75.57	169.0	
0.06505	13.7	23.29	42.931	-740.8	1.459	-740.9	5.502	5.508	1021.0	17015	.05877	280.2	75.98	168.1	
0.06084	13.6	23.28	42.950	-741.3	1.420	-741.5	5.371	5.377	1019.8	18074	.05533	278.5	76.40	167.0	
0.05685	13.5	23.27	42.969	-741.8	1.380	-742.0	5.243	5.248	1018.5	19213	.05205	276.7	76.83	166.0	
0.05308	13.4	23.26	42.989	-742.4	1.342	-742.5	5.117	5.122	1017.3	20441	.04892	274.9	77.26	165.0	
0.04951	13.3	23.25	43.007	-742.9	1.304	-743.0	4.992	4.997	1016.0	21765	.04594	273.1	77.69	163.9	
0.04614	13.2	23.24	43.026	-743.4	1.267	-743.5	4.870	4.874	1014.6	23194	.04311	271.3	78.13	162.9	
0.04296	13.1	23.23	43.045	-743.8	1.230	-743.9	4.750	4.754	1013.3	24738	.04042	269.5	78.58	161.8	
0.03996	13.0	23.22	43.063	-744.3	1.194	-744.4	4.631	4.635	1011.9	26407	.03787	267.6	79.03	160.7	
0.03713	12.9	23.21	43.082	-744.8	1.159	-744.8	4.514	4.518	1010.5	28215	.03544	265.7	79.49	159.6	
0.03447	12.8	23.20	43.100	-745.2	1.124	-745.3	4.400	4.403	1009.0	30173	.03314	263.8	79.96	158.4	
0.03197	12.7	23.19	43.118	-745.6	1.090	-745.7	4.287	4.290	1007.6	32298	.03096	261.9	80.43	157.3	
0.02962	12.6	23.18	43.135	-746.1	1.057	-746.1	4.176	4.179	1006.1	34606	.02890	260.0	80.90	156.2	
0.02741	12.5	23.17	43.153	-746.5	1.024	-746.5	4.067	4.070	1004.5	37114	.02694	258.1	81.39	155.0	
0.02534	12.4	23.16	43.170	-746.9	0.992	-746.9	3.960	3.963	1003.0	39845	.02510	256.1	81.88	153.8	
0.02340	12.3	23.15	43.188	-747.3	0.960	-747.3	3.855	3.858	1001.4	42821	.02335	254.2	82.38	152.6	
0.02158	12.2	23.15	43.205	-747.6	0.929	-747.7	3.751	3.753	999.8	46067	.02171	252.2	82.88	151.5	
0.01988	12.1	23.14	43.222	-748.0	0.899	-748.1	3.650	3.652	998.2	49613	.02016	250.2	83.40	150.3	
0.01830	12.0	23.13	43.238	-748.4	0.869	-748.4	3.550	3.552	996.6	53491	.01869	248.2	83.92	149.0	
0.01681	11.9	23.12	43.255	-748.7	0.839	-748.8	3.452	3.454	994.9	57738	.01732	246.2	84.45	147.8	
0.01543	11.8	23.11	43.271	-749.1	0.811	-749.1	3.356	3.358	993.2	62395	.01603	244.2	84.98	146.6	
0.01415	11.7	23.10	43.287	-749.4	0.783	-749.4	3.261	3.263	991.5	67509	.01481	242.1	85.53	145.4	
0.01295	11.6	23.09	43.303	-749.7	0.755	-749.8	3.169	3.170	989.8	73131	.01367	240.1	86.09	144.1	
0.01184	11.5	23.08	43.319	-750.0	0.728	-750.1	3.078	3.079	988.1	79321	.01261	238.1	86.65	142.9	
0.01081	11.4	23.08	43.335	-750.3	0.701	-750.4	2.989	2.990	986.3	86146	.01161	236.0	87.22	141.6	
0.00986	11.3	23.07	43.350	-750.6	0.676	-750.7	2.901	2.902	984.6	93682	.01067	233.9	87.81	140.4	
0.00898	11.2	23.06	43.366	-750.9	0.650	-750.9	2.815	2.816	982.8	102017	.00980	231.9	88.40	139.1	
0.00816	11.1	23.05	43.381	-751.2	0.625	-751.2	2.731	2.732	981.0	111248	.00899	229.8	89.00	137.8	
0.00741	11.0	23.04	43.396	-751.5	0.601	-751.5	2.649	2.650	979.2	121489	.00823	227.7	89.62	136.5	
0.00671	10.9	23.04	43.411	-751.7	0.577	-751.7	2.568	2.569	977.3	132869	.00753	225.6	90.24	135.3	
0.00607	10.8	23.03	43.425	-752.0	0.554	-752.0	2.489	2.490	975.5	145535	.00687	223.5	90.88	134.0	
0.00549	10.7	23.02	43.440	-752.2	0.531	-752.2	2.412	2.412	973.6	159656	.00626	221.4	91.52	132.7	
0.00495	10.6	23.01	43.454	-752.5	0.509	-752.5	2.336	2.336	971.8	175429	.00570	219.3	92.18	131.4	
0.00445	10.5	23.01	43.468	-752.7	0.487	-752.7	2.262	2.262	969.9	193077	.00518	217.2	92.86	130.1	
0.00400	10.4	23.00	43.482	-752.9	0.466	-752.9	2.189	2.189	968.0	212861	.00470	215.1	93.54	128.8	
0.00359	10.3	22.99	43.496	-753.1	0.445	-753.1	2.118	2.118	966.1	235082	.00425	213.0	94.24	127.5	
0.00321	10.2	22.98	43.509	-753.3	0.424	-753.3	2.048	2.048	964.2	260087	.00384	210.8	94.95	126.2	
0.00287	10.1	22.98	43.523	-753.5	0.405	-753.5	1.980	1.980	962.2	288284	.00347	208.7	95.68	124.9	
0.00256	10.0	22.97	43.536	-753.7	0.385	-753.7	1.914	1.914	960.3	320146	.00312	206.6	96.42	123.5	
3.00200	10.0		10.000	100.1	BERGERS U.UUU	y 100.1	1.011	1.011	000.0	320110	.00012	200.0	00.12	120.0	

^a McCarty et al. 1981

b Roder 1977

^c P = pressure

d atm = atmosphere (1 atm = 101.325 kPa)

e T = Temperature

 $^{^{}f}$ V = specific volume (V = 1/D)

g D = density

h H = enthalpy

S = entropy

^j U = internal energy

^k C_{sat} = specific heat at saturated solid

 C_p = specific heat at constant pressure

 $^{^{\}rm m}$ $\Delta H_{\rm sub}$ = enthalpy difference for sublimation

Table A1.3b — Thermodynamic properties of the hydrogen solid-vapor two phase region^{a, b, c}

				Solid phase				Vapor phase	
P ^d	T ^f	v ^{g,h}	н ⁱ	s ^k	C _{sat}	m ΔH _{sub}	z ⁿ	Н	S
mm Hg	К	cm /mol	cal/mol ^j	cal/mol · K	cal/mol · K	cal/mol	_	cal/mol	cal/mol · K
0.1917E+0I	10.0	22.873	1.4790000	0.1975000	0.5751000	230.55	0.99878	232.03	23.252
0.5343E+00	9.0	22.809	0.9788000	0.1450000	0.4280000	226.12	0.99956	227.10	25.269
0.1118E+00	8.0	22.754	0.6139000	0.1022000	0.3054000	221.53	1.00000	222.15	27.794
0.1561E-01	7.0	22.711	0.3598000	0.0684200	0.2065000	216.82	1.00000	217.18	31.043
0.1198E-02	6.0	22.678	0.1933000	0.0429100	0.1301000	212.02	1.00000	212.21	35.379
0.3570E-04	5.0	22.660	0.0927500	0.0247300	0.0742000	207.15	1.00000	207.24	41.455
0.2080E-06	4.0	22.650	0.0379900	0.0126600	0.0379900	202.24	1.00000	202.28	50.572
0.4832E-10	3.0	22.646	0.0120200	0.0053420	0.0160300	197.30	1.00000	197.31	65.771
0.3985E-17	2.0	22.645	0.0023740	0.0015830	0.0047490	192.34	1.00000	192.34	96.170
0.8255E-38	1.0	22.645	0.0001484	0.0001979	0.0005936	187.37	1.00000	187.37	187.372
d P = pressure e mm Hg = milling f T = Temperatur g V = specific vous h Ahlers 1963 i H = enthalpy j (cal/mol) x 2.07 k S = entropy l C _{sat} = specific m Δ H _{sub} = enthalp	er, and Kirk 1961 meter of mercury (ire olume (V = 1/dens	ity) solid ublimation	3322 kPa)						

	memicay	Tiarriic proper	tico or the rry		phase	acc region				Liquid phase		
P ^b	T ^d	V ^e	D ^f	Ha	Sh	Ui	ΔH _{fus} ^j	V	D	Н	S	U
atm	K	cm ³ /mol	mol/L	J/mol	J/mol · K	J/mol	J/mol	cm ³ /mol	mol/L	J/mol	J/mol · K	J/mol
0.0695	13.8	23.30	42.911	-740.2	1.500	-740.4	117.3	26.17	38.214	-622.9	10.00	-623.1
5.976	14.0	23.27	42.972	-724.9	1.595	-739.0	118.4	26.07	38.354	-606.6	10.05	-622.4
11.982	14.2	23.23	43.048	-709.5	1.685	-737.7	119.5	25.97	38.502	-590.0	10.10	-621.6
18.087	14.4	23.18	43.137	-693.9	1.771	-736.4	120.6	25.87	38.657	-573.3	10.15	-620.7
24.288	14.6	23.13	43.237	-678.1	1.854	-735.1	121.8	25.76	38.816	-556.4	10.19	-619.8
30.585	14.8	23.07	43.346	-662.2	1.933	-733.7	122.9	25.65	38.980	-539.3	10.24	-618.8
36.976	15.0	23.01	43.462	-646.2	2.008	-732.4	124.1	25.55	39.146	-522.1	10.28	-617.8
43.459	15.2	22.94	43.584	-630.0	2.079	-731.1	125.3	25.44	39.314	-504.7	10.32	-616.8
50.033	15.4	22.88	43.710	-613.8	2.145	-729.7	126.5	25.33	39.483	-487.2	10.36	-615.6
56.69	15.6	22.81	43.840	-597.4	2.208	-728.4	127.7	25.22	39.652	-469.6	10.40	-614.5
63.45	15.8	22.74	43.971	-580.9	2.267	-727.1	129.0	25.11	39.821	-451.9	10.43	-613.3
70.29	16.0	22.67	44.104	-564.3	2.321	-725.8	130.2	25.01	39.989	-434.0	10.46	-612.1
77.22	16.2	22.60	44.238	-547.6	2.372	-724.4	131.5	24.90	40.155	-416.0	10.49	-610.9
84.23	16.4	22.54	44.372	-530.8	2.419	-723.1	132.8	24.80	40.319	-397.9	10.52	-609.6
91.33	16.6	22.47	44.506	-513.9	2.463	-721.8	134.1	24.70	40.482	-379.7	10.54	-608.3
98.51	16.8	22.40	44.639	-496.8	2.504	-720.5	135.5	24.60	40.643	-361.4	10.57	-607.0
105.78	17.0	22.34	44.772	-479.7	2.543	-719.2	136.8	24.51	40.801	-342.9	10.59	-605.6
113.13	17.2	22.27	44.903	-462.5	2.578	-717.8	138.2	24.42	40.957	-324.4	10.61	-604.3
120.56	17.4	22.21	45.034	-445.2	2.612	-716.5	139.5	24.32	41.111	-305.7	10.63	-602.8
128.07	17.6	22.14	45.163	-427.8	2.644	-715.1	140.9	24.23	41.263	-286.9	10.65	-601.4
135.66	17.8	22.08	45.292	-410.3	2.673	-713.8	142.3	24.15	41.412	-268.0	10.67	-599.9
143.33	18.0	22.02	45.419	-392.6	2.702	-712.4	143.7	24.06	41.559	-248.9	10.69	-598.4
151.07	18.2	21.96	45.545	-374.9	2.728	-711.0	145.2	23.98	41.704	-229.7	10.70	-596.8
158.90	18.4	21.90	45.670	-357.0	2.753	-709.6	146.6	23.90	41.847	-210.4	10.72	-595.2
166.80	18.6	21.84	45.793	-339.1	2.777	-708.2	148.1	23.82	41.988	-191.0	10.74	-593.5
174.78	18.8	21.78	45.916	-321.0	2.801	-706.7	149.6	23.74	42.127	-171.4	10.76	-591.8
182.83	19.0	21.72	46.037	-302.8	2.824	-705.2	151.0	23.66	42.264	-151.8	10.77	-590.1
190.96	19.2	21.66	46.158	-284.5	2.847	-703.7	152.5	23.59	42.400	-132.0	10.79	-588.3
199.17	19.4	21.61	46.277	-266.1	2.870	-702.2	154.1	23.51	42.533	-112.0	10.81	-586.5
207.44	19.6	21.55	46.396	-247.5	2.892	-700.6	155.6	23.44	42.666	-91.9	10.83	-584.6

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215.79	19.8	21.50	46.514	-228.9	2.914	-699.0	157.1	23.37	42.796	-71.8	10.85	-582.7
224.22	20.0	21.45	46.631	-210.1	2.936	-697.3	158.7	23.30	42.925	-51.4	10.87	-580.7
232.71	20.2	21.39	46.747	-191.2	2.956	-695.7	160.3	23.23	43.053	-31.0	10.89	-578.7
241.28	20.4	21.34	46.863	-172.3	2.976	-694.0	161.8	23.16	43.180	-10.4	10.91	-576.6
249.92	20.6	21.29	46.978	-153.2	2.999	-692.2	163.4	23.09	43.305	10.3	10.93	-574.5
258.63	20.8	21.24	47.092	-133.9	3.020	-690.4	165.0	23.03	43.430	31.1	10.95	-572.3
267.41	21.0	21.18	47.206	-114.6	3.041	-688.6	166.7	22.96	43.553	52.0	10.98	-570.1
276.26	21.2	21.13	47.319	-95.2	3.063	-686.8	168.3	22.90	43.67S	73.1	11.00	-567.8
285.19	21.4	21.08	47.432	-75.6	3.084	-684.9	169.9	22.63	43.796	94.3	11.03	-565.5
294.18	21.6	21.03	47.544	-56.0	3.106	-682.9	171.6	22.77	43.916	l15.6	11.05	-563.1
303.23	21.8	20.98	47.656	-36.2	3.128	-681.0	173.3	22.71	44.036	137.1	11.08	-560.7
312.36	22.0	20.93	47.768	-16.3	3.150	-678.9	175.0	22.65	44.154	158.6	11.10	-558.2
321.56	22.2	20.89	47.879	3.6	3.173	-676.9	176.7	22.59	44.272	180.3	11.13	-555.7
330.82	22.4	20.84	47.990	23.7	3.195	-674.8	178.4	22.53	44.389	202.1	11.16	-553.1
340.15	22.6	20.79	48.101	43.9	3.218	-672.6	180.1	22.47	44.505	224.0	11.19	-550.4

a McCarty et al. 1981
b P = pressure
c atm = atmosphere (1 atm = 101.325 kPa)
d T = temperature
e V = specific volume (V = 1/D)
f D = density
g H = enthalpy
h S = entropy
i U = internal energy
j ΔH_{fus} = enthalpy difference for fusion

Table A1.5 — Molar volume (cm³/mol) of compressed solid para-hydrogen^a

Table A1.5 — Molai Volu	ine (em /mei) er	compressed se		<u>''</u>	
Pressure			Temperature		
(atm)			(K)		
(atm)	11.49	13.98	16.89	18.20	19.97
0	23.08				
25	22.63	22.83			
50	22.22	22.58			
75	21.85	22.24			
100	21.53	21.93			
150		21.26	22.00		
200			21.55	21.52	
250			21.10	21.07	21.45
300				20.70	21.30
350					21.15
McCarty et al. 1981					a.

Table A1.6 — Thermal expansion of solid para-hydrogen^a

Thermal Expansion coefficient, α x 10 ⁴
(1/K)
0.022
0.22
1.0
3.0
6.5
11.3
16.5
21.7
26.7
30.4
34.6
39.4
44.7
49.4

HYDROGEN - HYDROGEN, TECHNICAL MATERIAL SAFETY DATA SHEET

FSC: 6830

NIIN: (to be supplied by manufacturer)

Manufacturer's CAGE: (to be supplied by manufacturer)

Part No. Indicator: A

Part Number/Trade Name: HYDROGEN

General Information

Item Name: HYDROGEN, TECHNICAL

Company's Name: (to be supplied by manufacturer)
Company's Street: (to be supplied by manufacturer)
Company's City: (to be supplied by manufacturer)
Company's State: (to be supplied by manufacturer)
Company's Country: (to be supplied by manufacturer)
Company's Zip Code: (to be supplied by manufacturer)
Company's Emer Ph # (to be supplied by manufacturer)
Company's Info Ph #: (to be supplied by manufacturer)

Record No. For Safety Entry: 001 Tot Safety Entries This Stk#: 003

Status: SM

Date MSDS Prepared: (to be supplied by manufacturer) Safety Data Review Date: (to be supplied by manufacturer) Supply Item Manager: (to be supplied by manufacturer) MSDS Serial Number: (to be supplied by manufacturer) Specification Number: (to be supplied by manufacturer)

Spec Type, Grade, Class: TYPE I Hazard Characteristic Code: G2

Unit of Issue: CF

Unit of Issue Container Qty: (to be supplied by manufacturer)

Type of Container: CYLINDER
Net Unit Weight: UNKNOWN
NRC/State License Number: NONE
Net Propellant Weight-Ammo: NONE

Ingredients/Identity Information

Proprietary: NO

Ingredient: HYDROGEN

Ingredient Sequence Number: 01

%: 100

NIOSH (RTECS) Number: MW8900000

CAS Number: 1333-74-0

OSHA PEL: NOT ESTABLISHED ACGIH TLV: NOT ESTABLISHED

Other Recommended Limit: NONE RECOMMENDED

Figure A1.11 — Sample MSDS for gaseous and liquefied hydrogen

Physical/Chemical Characteristics Appearance And Odor: COLORLES GAS AT NORMAL TEMPERATURE AND PRESSURE; **ODORLESS** Boiling Point: -422F,-252C Melting Point: -434F,-259C Vapor Pressure (MM Hg/70 F): GAS Vapor Density (Air = 1): 0.696 Specific Gravity: GAS **Decomposition Temperature: UNKNOWN** Evaporation Rate and Ref: N/A Solubility in Water: NEGLIGIBLE Viscosity: UNKNOWN Corrosion Rate (IPY): UNKNOWN Autoignition Temperature: 968F _____ Fire and Explosion Hazard Data Flash Point: FLAMMABLE GAS Lower Explosive Limit: 4 Upper Explosive Limit: 75 Extinguishing Media: CO2, DRY CHEMICALS, WATER SPRAY OR FOG Special Fire Fighting Proc: EVACUATE AREA. COOL CONTAINER W/WATER SPRAY (MAX DISTANCE). DO NOT EXTINGUISH FLAMES, ALLOW TO BURN OUT! USE SCBA. STOP GAS FLOW & REMOVE CONTAINERS IF W/O RISK Unusual Fire And Expl Hazrds: FLAME NEARLY INVISIBLE. FORMS EXPOLSIVE MIXTURES W/AIR & OXIDIZERS. KEEP CONTAINERS BELOW 125F. ESCAPING GAS MAY IGNITE SPONTANEOUSLY, HAS LOW IGNITION ENERGY. Reactivity Data Stability: YES Cond to Avoid (Stability): FOLLOW COMPRESSED GAS ASSN INSTRUCTIONS IN PAMPHLET "SAFE HANDLING OF COMPRESSED GAS IN CONTAINERS". Materials to Avoid: OXIDIZING AGENTS, LITHIUM, HALOGENS Hazardous Decomp Products: NONE Hazardous Poly Occur: NO Conditions to Avoid (Poly): WILL NOT OCCUR. _____ Health Hazard Data LD50-LC50 Mixture: LD50 (ORAL RAT) IS UNKNOWN Route of Entry - Inhalation: YES Route of Entry - Skin: NO Route of Entry - Ingestion: NO Health Haz Acute And Chronic: INGESTED:UNLIKELY ROUTE OF EXPOSURE. SKIN:NO EVIDENCE OF ADVERSE EFFECTS. INHALED:SIMPLE ASPHYXIANT. MODERATE CONCENTRATIONS. MAY CAUSE HEADACHE, DROWSINESS, EXCITATION, EXCESS SALIVATION, VOMITING & UNCONSCIOUSNESS. EYE:NO EVIDENCE OF ADVERSE EFFECTS. Carcinogenicity - NTP: NO Carcinogenicity - IARC: NO Carcinogenicity - OSHA: NO

Figure A1.11 — Sample MSDS for gaseous and liquefied hydrogen (continued)

Explanation Carcinogenicity: MFR LISTED NO INFORMATION ABOUT THE

CARCINOGENICITY OF THIS MATERIAL. HMIS DOES NOT EXPECT IT TO BE CARCINOGENIC.

Signs/Symptoms Of Overexp: INGESTED:UNLIKELY ROUTE OF EXPOSURE. SKIN:NO EVIDENCE OF ADVERSE EFFECTS. INHALED:SIMPLE ASPHYXIANT. HEADACHE, NO EVIDENCE OF ADVERSE EFFECTS.

Med Cond Aggravated By Exp: A KNOWLEDGE OF THE AVAILABLE TOXICOLOGY INFORMATION AND OF THE PHYSICAL & CHEMICAL PROPERTIES OF THE MATERIAL SUGGEST THAT OVEREXPOSURE IS UNLIKELY TO AGGRAVATE EXISTING MEDICAL CONDITIONS. Emergency/First Aid Proc: INGESTED:PRODUCT IS A GAS AT NORMAL TEMPERATURE & PRESSURE. SKIN:WASH WITH SOAP & WATER. INHALED:REMOVE TO FRESH AIR. GIVE OXYGEN IF BREATHING IS DIFFICULT, ARTIFICIAL RESPIRATION IF NOT BREATHING. GET IMMEDIATE MEDICAL ATTENTION. EYE:FLUSH W/WATER. NOTE TO PHYSICIAN:THERE IS NO SPECIFIC ANTIDOTE. PRODUCT IS RELATIVELY INERT. TREATMENT SHOULD CONTROL SYMPTOMS AND CLINICAL CONDITION.

Precautions for Safe Handling and Use

Steps if Matl Released/Spill: DANGER! FORMS EXPLOSIVE MIXTURES W/AIR! EVACUATE AREA. USE SCBA. REMOVE SOURCES OF IGNITION IF W/O RISK. STOP LEAK IF W/O RISK. VENTILATE AREA OR MOVE CONTAINER TO WELL-VENTILATED AREA IF W/O RISK. CHECK ATMOSPHERE FOR EXPLOSIVENESS BEFORE ENTERING.

Neutralizing Agent: NO INFORMATION GIVEN BY MFR ON MSDS.

Waste Disposal Method: PREVENT WASTE FROM CONTAMINATING SURROUNDING ENVIRONMENT. DISCARD ANY PRODUCT, RESIDUE, DISPOSABLE CONTAINER OR LINER IN AN ENVIRONMENTALLY ACCEPTABLE MANNER IN FULL COMPLIANCE FEDERAL, STATE & LOCAL REGULATIONS.

Precautions-Handling/Storing: FOLLOW COMPRESSED GAS ASSN INSTRUCTIONS IN PAMPHLET "SAFE HANDLING OF COMPRESSED GAS IN CONTAINERS". NEVER WORK ON A PRESSURIZED SYSTEM.

Other Precautions: PROTECT CYLINDERS FROM DIRECT SUNLIGHT & STORE IN A WELL VENTILATED AREA. PROTECT FROM PHYSICAL DAMAGE. ISOLATE CYLINDERS FROM OXYGEN & CHLORINE. DO NOT LOAD WITH EXPLOSIVES, POISONS, RADIOACTIVE MATERIALS & ORGANIC PEROXIDES.

Control Measures

Respiratory Protection: NONE REQUIRED UNDER NORMAL USE. HOWEVER AIR SUPPLIED RESPIRATORS ARE REQUIRED WHILE WORKING IN CONFINED SPACES WITH THIS PRODUCT. THE RESPIRATORY PROTECTION USE MUST CONFORM WITH OSHA RULES IN 29 CFR1910.134.

Ventilation: USE EXPLOSION PROOF GENERAL/LOCAL EXHAUST SUFFICIENT TO CONTROL WORKER EXPOSURE.

Protective Gloves: PREFERRED FOR CYLINDER HANDLING

Eye Protection: SELECT PER OSHA 29CFR1910.133

Other Protective Equipment: METATARSAL SHOES FOR CYLINDER HANDLING. SELECT

PER OSHA 29CFR1910.132 & 1910.133.

Work Hygienic Practices: MFR: ? HMIS:USE GOOD INDUSTRIAL HYGIENE PRACTICE.

AVOID UNNECESSARY EXPOSURE. WASH THOROUGHLY BEFORE EATING OR DRINKING

Suppl. Safety & Health Data: NONE

Figure A1.11 — Sample MSDS for gaseous and liquefied hydrogen (continued)

Transportation Data Trans Data Review Date: 94365 DOT PSN Code: HLR DOT Proper Shipping Name: HYDROGEN, COMPRESSED DOT Class: 2.1 DOT ID Number: UN1049 DOT Label: FLAMMABLE GAS IMO PSN Code: IGH IMO Proper Shipping Name: HYDROGEN, COMPRESSED IMO Regulations Page Number: 2148 IMO UN Number: 1049 IMO UN Class: 2(2.1) IMO Subsidiary Risk Label: -IATA PSN Code: NSD IATA UN ID Number: 1049 IATA Proper Shipping Name: HYDROGEN, COMPRESSED IATA UN Class: 2.1 IATA Label: FLAMMABLE GAS AFI PSN Code: NSD AFI Symbols: 0 AFI Prop. Shipping Name: HYDROGEN, COMPRESSED AFI Class: 2.1 AFI ID Number: UN1049 AFI Label: FLAMMABLE GAS AFI Basic Pac Ref: 6-6,6-10 Disposal Data _____ Label Data Label Required: YES Technical Review Date: 31DEC94 MFR Label Number: NONE Label Status: F Common Name: HYDROGEN Signal Word: DANGER! Acute Health Hazard-Slight: X Contact Hazard-Slight: X Fire Hazard-Severe: X Reactivity Hazard-None: X Special Hazard Precautions: **TARGET ORGANS:RESPIRATORY SYSTEM** INGESTED: UNLIKELY ROUTE OF EXPOSURE. SKIN: NO EVIDENCE OF ADVERSE EFFECTS. INHALED:SIMPLE ASPHYXIANT, MODERATE CONCENTRATIONS MAY CAUSE HEADACHE. DROWSINESS, EXCITATION, EXCESS SALVATION, VOMITING & UNCONSCIOUSNESS.

Figure A1.11 — Sample MSDS for gaseous and liquefied hydrogen (continued)

EYE:NO EVIDENCE OF ADVERSE EFFECTS.

FOLLOW COMPRESSED GAS ASSN INSTRUCTIONS IN DANGER! FORMS EXPLOSIVE MIXTURES W/AIR! EVACUATE AREA, USE SCBA. REMOVE SOURCES OF IGNITION & STOP LEAK IF W/O RISK.

VENTILATE AREA OR MOVE CONTAINER TO WELL VENTILATED AREA IF W/O RISK. CHECK ATMOSPHERE FOR EXPLOSIVENESS ENTERING AREA.

Protect Eye: Y Protect Skin: Y

Label Name: (to be supplied by manufacturer)
Label Street: (to be supplied by manufacturer)
Label City: (to be supplied by manufacturer)
Label State: (to be supplied by manufacturer)
Label Zip Code: (to be supplied by manufacturer)
Label Country: (to be supplied by manufacturer)

Label Emergency Number: (to be supplied by manufacturer)

LIQUID HYDROGEN - CRYOGENIC LIQUID MATERIAL SAFETY DATA SHEET

FSC: 9135

NIIN: (to be supplied by manufacturer)

Manufacturer's CAGE: (to be supplied by manufacturer)

Part No. Indicator: A

Part Number/Trade Name: LIQUID HYDROGEN

General Information

Item Name: CRYOGENIC LIQUID

Company's Name: (to be supplied by manufacturer)
Company's Street: (to be supplied by manufacturer)
Company's City: (to be supplied by manufacturer)
Company's State: (to be supplied by manufacturer)
Company's Country: (to be supplied by manufacturer)
Company's Zip Code: (to be supplied by manufacturer)
Company's Emerg Ph #: (to be supplied by manufacturer)
Company's Info Ph #: (to be supplied by manufacturer)

Record No. For Safety Entry: 001 Tot Safety Entries This Stk#: 002

Status: SE

Date MSDS Prepared: (to be supplied by manufacturer) Safety Data Review Date: (to be supplied by manufacturer) Preparer's Company: (to be supplied by manufacturer) Preparer's St or P. O. Box: (to be supplied by manufacturer)

Preparer's City: (to be supplied by manufacturer)
Preparer's State: (to be supplied by manufacturer)
Preparer's Zip Code: (to be supplied by manufacturer)
MSDS Serial Number: (to be supplied by manufacturer)

Ingredients/Identity Information

Proprietary: NO

Ingredient: HYDROGEN

Ingredient Sequence Number: 01

%: 100

NIOSH (RTECS) Number: MW8900000

CAS Number: 1333-74-0

ACGIH TLV: SIMPLE ASPHYXIANT

Figure A1.11 — Sample MSDS for gaseous and liquefied hydrogen (continued)

Physical/Chemical Characteristics Appearance And Odor: COLORLESS, ODORLESS CRYOGENIC LIQUID. Boiling Point: -422.99F Melting Point: -434.6F Vapor Density (Air=1): 0.0696 Specific Gravity: 0.07 Evaporation Rate And Ref: (BU AC =1): >3 Solubility In Water: NEGLIGIBLE % Volatiles By Volume: 100 Autoignition Temperature: 968F Fire and Explosion Hazard Data Flash Point: FLAMMABLE GAS Lower Explosive Limit: 4 Upper Explosive Limit: 75 Extinguishing Media: CO2, DRY CHEMICAL, WATER SPRAY/FOG. Special Fire Fighting Proc: EVACUATE AREA. IMMEDIATELY COOL CONTAINERS W/WATER SPRAY FROM MAXIMUM DISTANCE W/O EXTINGUISHING FLAMES. REMOVE ALL IGNITION SOURCES SAFELY. WEAR SCBA WHERE NEEDED. SAFELY STOP LEAK WHILE COOLING W/WATER SPRAY. SAFELY REMOVE ALL CONTAINERS FROM AREA. ALLOW FIRE TO BURN OUT. Unusual Fire And Expl Hazrds: MAY FORM EXPLOSIVE MIXTURES W/AIR & OXIDIZING AGENTS. LIQUID WILL SOLIDIFY AIR & CREATE EXPLOSION HAZARD. CONTAINER MAY RUPTURE DUE TO HEAT OF FIRE. FLAME ALMOST INVISIBLE. FIREBALL IS FORMED IF GAS CLOUD IS IGNITED. EXPLOSIVE ATMOSPHERES MAY LINGER. Reactivity Data Stability: YES Cond to Avoid (Stability): HEAT, FIRE & OTHER IGNITION SOURCES. Materials to Avoid: OXYGEN, OXIDIZING AGENTS, AIR, LITHIUM, HALOGENS. Hazardous Decomp Products: NONE Hazardous Poly Occur: NO Health Hazard Data Route of Entry - Inhalation: YES Route of Entry - Skin: NO Route of Entry - Ingestion: YES Health Haz Acute And Chronic: INGESTION: CONTACT W/LIQUID MAY CAUSE FROSTBITE OF LIPS & MOUTH. EYES/SKIN: LIQUID CONTACT MAY CAUSE FROSTBITE. INHALATION: ASPHYXIANT. CAN CAUSE RAPID SUFFOCATION/DEATH DUE TO OXYGEN DEFICIENCY. Carcinogenicity - NTP: NO

Explanation Carcinogenicity: NONE Signs/Symptoms of Overexp: HEADACHE, DROWSINESS, DIZZINESS, EXCITATION, EXCESS SALIVATION, VOMITING, UNCONSCIOUSNESS.

Emergency/First Aid Proc: SKIN: IMMEDIATELY WARM FROSTBITE AREA W/WARM

Carcinogenicity - IARC: NO Carcinogenicity - OSHA: NO

WATER. DON'T EXCEED 105F. INHALATION: REMOVE TO FRESH AIR. GIVE CPR/OXYGEN IF EYES: IMMEDIATELY FLUSH W/WATER FOR 15 MIN. OBTAIN MEDICAL ATTENTION IN ALL CASES. NOTE TO PHYSICIAN: NO SPECIFIC ANTIDOTE. PRODUCT IS RELATIVELY INERT. TREATMENT OF OVEREXPOSURE SHOULD BE DIRECTED AT CONTROL OF SYMPTOMS & CLINICAL CONDITION. ______ Precautions for Safe Handling and Use Steps if Matl Released/Spill: IMMEDIATELY EVACUATE AREA. WEAR SCBA WHERE NEEDED. REMOVE IGNITION SOURCES. REDUCE VAPORS W/FOG/FINE WATER SPRAY. BEFORE ENTERING AREA, CHECK ATMOSPHERE W/APPROPRIATE DEVICE. VENTILATE AREA/MOVE LEAKING CONTAINER TO WELL-VENTILATED AREA SAFELY. Waste Disposal Method: PREVENT WASTE FROM CONTAMINATING SURROUNDING ENVIRONMENT. DISCARD ANY PRODUCT/RESIDUE/DISPOSABLE CONTAINER/LINER IN AN ENVIRONMENTALLY ACCEPTABLE MANNER IAW/FEDERAL, STATE & LOCAL REGULATIONS. SAFELY SHUT OFF LEAK. Precautions-Handling/Storing: STORE & USE W/ADEQUATE VENTILATION AT ALL TIMES. USE ONLY IN CLOSED SYSTEM. CLOSE VALVE WHEN NOT IN USE/WHEN EMPTY. KEEP AWAY FROM OXIDIZING AGENTS. Other Precautions: DON'T GET LIQUID IN EYES, ON SKIN/CLOTHING. USE PIPING & EQUIIPMENT DESIGNED TO WITHSTAND PRESSURES/TEMPS TO BE ENCOUNTERED. ONLY USE SPARK/EXPLOSION PROOF EQUIPMENT. GROUND ALL EQUIPMENT. NEVER WORK ON A PRESSURIZED SYSTEM. Control Measures Respiratory Protection: NONE REQUIRED UNDER NORMAL USE. WEAR AIR SUPPLIED RESPIRATOR WHILE WORKING IN CONFINED AREAS W/THIS PRODUCT. Ventilation: EXPLOSION PROOF LOCAL EXHAUST SYSTEM W/SUFFICIENT AIR FLOW VELOCITY RECOMMENDED. GENERAL EXHAUST MAY BE ACCEPTABLE. Protective Gloves: LOOSE FITTING CRYOGENIC Eve Protection: SAFETY GLASSES & FULL FACE SHIELD Other Protective Equipment: METATARSAL SHOES FOR CYLINDER HANDLING, CUFFLESS TROUSERS OUTSIDE SHOES, HIGH TOP SHOES ARE PREFERRED. Work Hygienic Practices: REMOVE/LAUNDER CONTAMINATED CLOTHING BEFORE REUSE. Suppl. Safety & Health Data: NONE **Transportation Data**

Figure A1.11 — Sample MSDS for gaseous and liquefied hydrogen (continued)

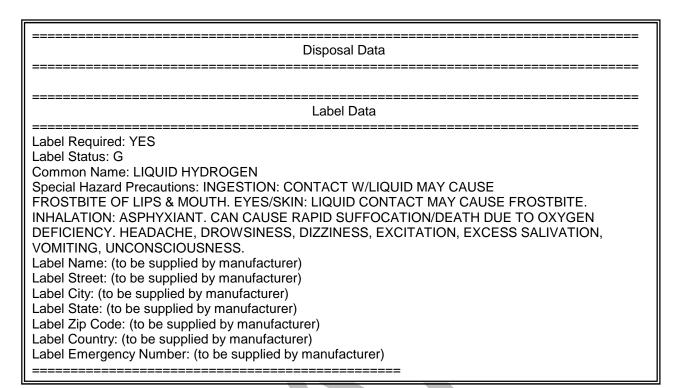


Figure A1.11 — Sample MSDS for gaseous and liquefied hydrogen (continued)

A.2 Flammability, Fires, Deflagration, and Detonation

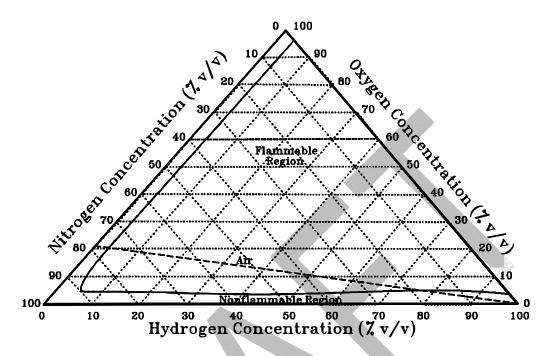


Figure A2.1 — Flammability limits at a pressure of 101.3 kPa (14.7 psia) and a temperature of 298 K (77 °F) (Coward and Jones 1952; Payman and Titman 1936)

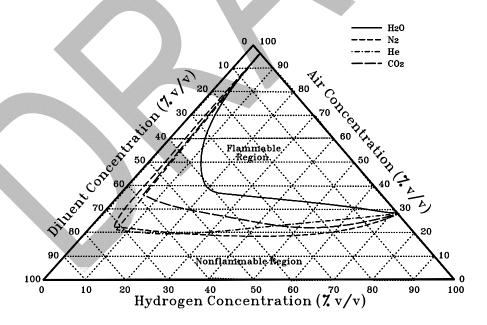


Figure A2.2 — Effects of N_2 , He, and CO_2 diluents at 298 K (77 °F), and H_2O diluent at 422 K (300 °F) on flammability limits of hydrogen in air at 101.3 kPa (14.7 psia) (Coward and Jones 1952; Jones and Perrott 1927; Coley and Field 1973)

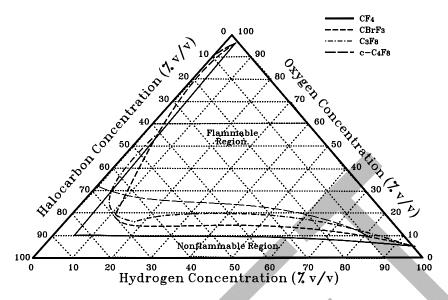


Figure A2.3 — Effects of halocarbon inhibitors on flammability limits of hydrogen-oxygen mixtures at a pressure of 101.3 kPa (14.7 psia) and a temperature of 298 K (77 °F) (McHale, Geary, von Elbe, and Huggett 1971)

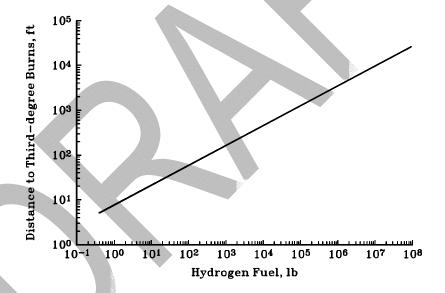


Figure A2.4 — Distance for fireball radiation flux induced third degree burns per amount of fuel burned at a thermal radiation intensity of 134 kJ/m² (11.8 Btu/ft²) (Siegel and Howell 1971)

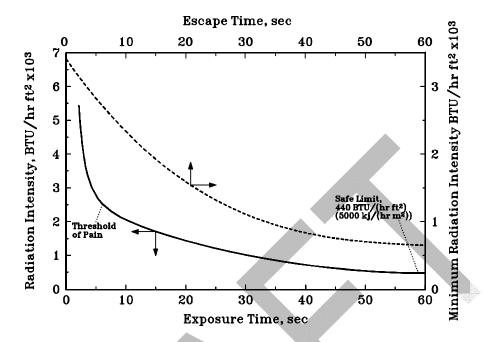


Figure A2.5 — Radiation intensity as a function of exposure time or escape time (Kent 1968)

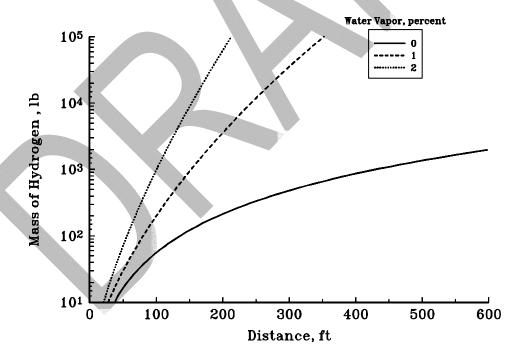


Figure A2.6 — Variation in distance from a hydrogen fire for a thermal radiation exposure of 2 cal/cm² for an exposure duration of 10 s (Zebetakis and Burgess 1961). 2 cal/cm² is roughly the radiant flux required to produce flesh burns and ignite certain combustible materials in short exposure times. 2 cal/cm² = 8.4 J/cm² (0.051 Btu/in²)

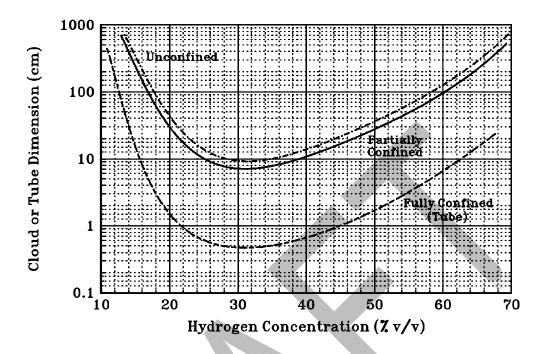


Figure A2.7 — Minimum dimensions of GH_2 -air mixtures for detonation at 101.3 kPa (14.7 psia) and 298 K (77 °F) (Lee, Kynstantus, Guirao, Benedick, and Shepherd 1982)

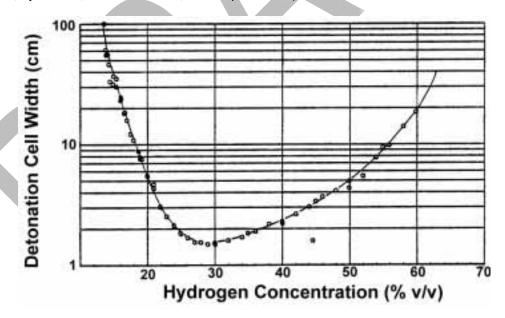


Figure A2.8 — Detonation cell widths for hydrogen-air mixtures at 101.3 kPa (14.7 psia) (Lee, Kynstantus, Guirao, Benedick, and Shepherd 1982)

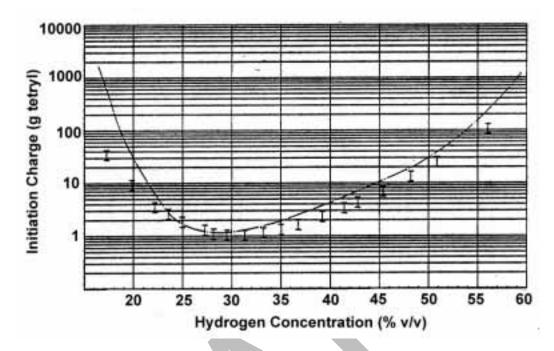


Figure A2.9 — Minimum initiation energy for direct detonation of hydrogen-air mixtures (Lee, Kynstantus, Guirao, Benedick, and Shepherd 1982)

Table A2.1 — Potential ignition sources

Electrical sources	Mechanical sources	Thermal sources	Chemical sources
Static discharge	Mechanical impact	Open flame	Catalysts
Static electricity (two- phase flow, for example)	Tensile rupture	Hot surface	Reactants
Static electricity (e.g., flow with solid particles included)	Friction and galling	Personnel smoking	
Electric arc	Mechanical vibration	Welding	
Lightning	Metal fracture	Exhaust from combustion engine	
Charge accumulation		Resonance ignition	
Electric charge generated by equipment operation		Explosive charge	
Electrical short circuits		High-velocity jet heating	
Electrical sparks		Shock wave from tank rupture	
Clothing (static electricity)		Fragment from bursting tank	
a This list should not be	viewed as a complete list. B	e alert for other possible ignitior	sources.

Table A2.2 — Flammability limits^a

Conditions	Hydrogen Content vol%						
	Upper pro	pagation	Downward prop	pagation	Horizontal propagation		
	Lower limit	Upper limit	Lower limit	Upper limit	Lower limit	Upper limit	
Hydrogen in air and ox	Hydrogen in air and oxygen at 101.3 kPa (14.7 psia):						
H ₂ + air:							
Tubes	4.1	74.8	8.9	74.5	6.2	71.3	
Spherical Vessels	4.6	75.5					
H ₂ + oxygen	4.1	94.0	4.1	92.0			
Hydrogen plus inert ga	as mixtures at	101.3 kPa (1	4.7 psia):				
H ₂ +He+21 vol% O ₂	7.7	75.7	8.7	7 5.7			
H ₂ +CO ₂ +21 vol% O ₂	5.3	69.8	13.1	69.8			
H ₂ +N ₂ +21 vol% O ₂	4.2	74.6	9.0	74.6			
Hydrogen in air at redu	uced pressure	with a 45 mJ	(47.5 Btu) ignition sou	ırce:			
Pressure	25 cm	Tube	2 L Sphe	re			
kPa							
	Lower limit	Upper limit	Lower limit	Upper limit			
20	≈ 4	≈ 56	≈ 5	≈ 52			
10	≈ 10	≈ 42	≈ 11	≈ 35			
7	≈ 15	≈ 33	≈ 16	≈ 27			
6							
Note: Dashes indicate	no informatio	n available.					
^a Benz, Bishop, and Pe	dley 1988						

Table A2.3 — Effects of diluents on flammable range for hydrogen in air b

Tube diameter cm (in.)	Rating of diluents at reducing flammable range				
Wide tubes	CO ₂ <n<sub>2 <he <ar<sup="">c</he></n<sub>				
2.2 (0.87)	CO_2 <he <n<sub="">2 <ar<sup>c</ar<sup></he>				
1.6 (0.63)	He $\langle CO_2 \langle N_2 \rangle \langle Ar^c \rangle$				

a Equal concentrations
b Mellish and Linnett 1953
c Ar is the least effective in reducing the flammable range

Table A2.4 — Inhibitor for extinction of hydrogen diffusion flames^a

Inhibitor	Concentration at flame extinction vol%
Added to air:	
Nitrogen	94.1
CH₃Br	11.7
CBrF ₃	17.7
Added to fuel:	
Nitrogen	52.4
CH₃Br	58.1
BrCF ₃	56.6
^a Creitz 1961. Results based	on physical observation

Table A2.5 — Critical radiant flux levels^a

Table 712.6 Cittlear radial	
Radiant flux	Effect
W/cm ² (Btu/h/ft ²)	
,	
0.473 (1,500)	Pain felt in 15-30 s (skin burns in 30 s)
1.167 (3,700)	Thin steel with insulated backing can undergo
	failure
1.260 (4,000)	Minimum flux - wood ignition
2.30 (7,300)	Uninsulated steel - undergoes structural failure
5.86 (18,000)	Fiber insulating board - ignition after 3 s exposure
4.35 (14,000)	Fiber insulating board - ignition after 7 s exposure
3.35 (11,000)	Cotton fabrics - ignition after 7 s exposure
NOTE 1	
	2

Safe limit for extended exposure: ≈ 0.139 W/cm² (440 Btu/h/ft²). NOTE 2

- Burns for exposure for 10-30 s: 1st degree burn \approx 2-4 cal/cm² or 8.4-16.7 J/cm² (0.0051-0.102 Btu/in²) 2nd degree burn \approx 4-8 cal/cm² or 16.7-33.5 J/cm² (0.102-0.204 Btu/in²)
- ^a Ordin 1983

Table A2.6 — Hydrogen-air flammability^a

LFL %v/v	Other %v/v	UFL %v/v	Pressure kPa (psia)	Temperature (K)	Confinement Tube Size Diameter (cm)	Flame Direction	Ignition Energy	Note
6	22 ^b	79	0.12 ^b (0.017)	NA	182 and 366	NA	200–1200 J	С
4	24 ^b	64	6.9 ^b (1)	311 (100 °F)	25	Central ignition	45 mJ 4.27x10 ⁻⁵ Btu	d
4.1	29.6 ^e	75	101.3 (14.7)	Room ^f temperature	7.5	upward	17 աJ ^g	h
9.4	-	71.5	101.3 (14.7)	290 (63 °F)	2.5	downward	NA ⁱ	h
6.3	-	81.5	101.3 (14.7)	673 (752 °F)	2.5	downward	NA ⁱ	h
10.2	-	68.5	1000 (145)	298	7.6	Central ignition	NA i	h
9	-	75	12500 (1814)	298	7.6	Central ignition	NA	h

- Benz, Bishop and Pedley, 1988
- Low Pressure Limit where UFL and LFL meet Thomson and Enloe, 1966
- Mills, Linley, and Pippen, 1977 Stoichiometric Mixture
- Coward and Jones do not provide a specific value, but state that the normal variation of room temperatures have no effect on flammability limits.
- Minimum Ignition Energy (MIE)
- Coward and Jones, 1952
- The ignition energy used in these experiments was well above the MIE.

Table A2.7 Hydrogen-oxygen flammability^a

LFL %v/v	Other %v/v	UFL %v/v	Pressure kPa (psia)	Temperatur e (K)	Confinement Tube Size Diameter (cm)	Flame Direction	Ignition Energy	Note
5	30-60 b	97	0.06 ^b (0.009)	NA	182 and 366	NA	200–1200 J	С
NA	28-78 ^b	95	1.0 ^b (0.15)	NA	56	Central ignition	10 J	d
3.9	66.6 ^e	95.7	101.3 (14.7)	Room ^f temperature	4.5	upward	8 µJ ^ց	h
9.6	1	90.9	101.3 (14.7)	288 (58 °F)	35 ml sphere	horizontal	NA ⁱ	h
9.1	-	94.0	101.3 (14.7)	573 (572 °F)	35 ml sphere	horizontal	NA ⁱ	h
8-9	-	95.7 ^J	12361 (1793)	Room ^f temperature	7.6	downward	NA ⁱ	h

Benz, Bishop and Pedley, 1988 Low Pressure Limit where UFL and LFL meet

Thomson and Enloe, 1966

Benz and Boucher, 1982

Stoichiometric Mixture

Coward and Jones do not provide a specific value, but state that the normal variation of room temperatures have no effect on flammability limits.

Minimum Ignition Energy

Coward and Jones, 1952

The ignition energy used in these experiments was well above the minimum ignition energy (MIE). Reported by Straus et. al., 1961 for a pressure of 1520 kPa (221 psia)

Hydrogen Storage Siting A.3

Table A3.1 — Order of preference for location of GH₂ storage systems^{a, b}

		GH ₂ volume	
Nature of location	Less than 3000 ft ³ (85 m ³)	3000 to 15000 ft ³ (85 to 425 m ³)	Over 15000 ft ³ (425 m³)
Outdoors			
In separate building	II	II	
In special room	III	III	Not permitted
Inside buildings, but not in a special room and exposed to other occupancies	IV	Not permitted	Not permitted

 ^a 29 CFR 1910.103 and NFPA 50A
 ^b The location of GH₂ storage, as determined by the maximum total quantity of GH₂, shall be in the order of preference indicated by Roman numerals with I indicating the most preferred and IV the least preferred location.

Table A3.2 — QD requirements for nonpropellant GH₂ systems for outdoor locations^a

rable A3.2 — QD requirem	ients for nonpropellant GH ₂ sys	stems for outdoor locations				
		Size of gaseous hydrogen system				
Type of outd	loor exposure ^{g, h}	Less than	3,000 CF (85 CM)	In Excess		
. , , , , , , , , , , , , , , , , , , ,	on on product		to (435 CM)	of		
		3000 CF ⁱ (85 CM ^j)	15000 CF (425 CM)	15000 CF (425 CM)		
	a) Wall(s) adjacent to system					
	constructed of noncombustible or limited-combustible					
	materials.					
	Sprinklered building or structure,					
	or contents noncombustible.	0 _p	5 ft (1.5 m) ^b	5 ft (1.5 m) ^b		
Building or structure	Unsprinklered building or	0	3 it (1.5 iii)	3 it (1.3 iii)		
1. Duliding of structure	structure with combustible					
	contents.					
	Adjacent wall(s) with fire-resistance		A 337			
	rating less than	d		۵		
	2 h	0 ^d	10 ft (3 m)	25 ft (7.6 m) ^e		
	Adjacent wall(s) with fire-resistance					
	rating of 2 h or greater. c	0	5 ft (1.5 m)	5 ft (1.5 m)		
	b) Wall(s) adjacent to system	0	311 (1.5111)	311 (1.5111)		
	constructed of other than					
	noncombustible or limited					
	materials.	10 ft (3 m)	25 ft (7.6 m)	50 ft (15 m) ^e		
2. Wall openings	Not above any part of a system	10 ft (3 m)	10 ft (3 m)	10 ft (3 m)		
·	Above any part of a system	25 ft (7.6 m)	25 ft (7.6 m)	25 ft (7.6 m)		
All classes of flammable	0 – 1,000 gal (3785 L)	10 ft (3 m)	10 ft (3 m)	10 ft (3 m)		
and combustible liquids above ground.	In excess of 1,000 gal (3785 L)			<u> </u>		
above ground.	in excess of 1,000 gai (0700 L)	25 ft (7.6 m)	25 ft (7.6 m) ^f	25 ft (7.6 m) ^T		
All classes of flammable	Tank	10 ft (3 m)	10 ft (3 m)	10 ft (3 m) ^f		
and combustible liquids			, ,	` ′		
below ground — 0-1000 gal (0-3785 L)	Vent or fill opening of tank	25 ft (7.6 m) [†]	25 ft (7.6 m) [†]	25 ft (7.6 m) [†]		
5. All classes of flammable	Tank		20 ft (6 m) [†]	20 ft (6 m) ^f		
and combustible liquids		20 ft (6 m)	20 π (6 m)	20 π (6 m)		
below ground - in excess		25 ft (7.6 m) ^f	25 ft (7.6 m) ^f	25 ft (7.6 m) ^f		
of 1000 gal (3785 L)	Vent or fill opening of tank					
6. Flammable gas storage	0-15,000 CF (255 CM) capacity	10 ft (3 m)	25 ft (7.6 m)	25 ft (7.6 m)		
(other than hydrogen), high pressure or low pressure.	In excess of 15,000 CF (255 CM)	25 ft (7.6 m)	50 ft (15 m)	50 ft (15 m)		
pressure of low pressure.	capacity	25 11 (7.5 111)	30 11 (13 111)	30 11 (13 111)		
7. Oxygen storage	20,000 CF (566 CM) or less	Refer to NFPA 51		•		
	More than 20,000 CF (566 CM)	Refer to NFPA 50	T			
8. Fast burning solids such as on		50 ft (15 m)	50 ft (15 m)	50 ft (15 m)		
9. Slow burning solids such as he	eavy timber or coal	25 ft (7.6 m)	25 ft (7.6 m) 25 ft (7.6 m)	25 ft (7.6 m)		
10. Open flames and welding	ets to ventilating or air- conditioning	25 ft (7.6 m)	Z3 IL (7.0 III)	25 ft (7.6 m)		
equipment	old to verificating of an - conditioning	50 ft (15 m)	50 ft (15 m)	50 ft (15 m)		
12. Places of public assembly		25 ft (7.6 m)	25 ft (7.6 m)	25 ft (7.6 m)		
13. Public sidewalks and parked	vehicles	15 ft (4.6 m)	15 ft (4.6 m)	15 ft (4.6 m)		
14. Line of adjoining property wh	ich may be built upon	5 ft (1.5 m)	5 ft (1.5 m)	5 ft (1.5 m)		

a NFPA 50A

^c Exclusive of windows and doors

^e But not less than one half the height of adjacent wall or building or structure

ⁱ CF = cubic feet @ 101.3 kPa (14.7 psia) and 294 K (70 °F)

Portions of wall less than 10 ft (3 m) (measured horizontally) from any part of a system shall have a fire-resistance rating of at least one-half hour.

d Portions of walls less than 10 ft (3 m) (measured horizontally) from any part of a system shall have a fire resistance rating of at least 1 h.

Distances may be reduced to 15 ft (4.6 m) for Class IIIB combustible liquids. Class IIIB liquids include those having a closed cup flash point at or above 200 °F (366.5 K).

The distances in exposure types 1, 3 through 10, and 14 shall not apply where protective structures having a minimum fire-resistance rating of 2 h are located between the system and exposure.

h Unloading connections on delivery equipment shall not be positioned closer to any of the exposures cited than the distances given for the storage system.

¹ CM = cubic meters @ 101.3 kPa (14.7 psia) and 294.1 K (70 °F)

Table A3.3 — Order of preference for location of LH₂ storage systems^{a, b, c}

	LH ₂ volume				
Nature of Location	150 L to 189 L (39.6 gal to 50 gal)	190 to 1136 L (51 gal to 3,000 gal)	1137 L to 2271 L (301 gal to 600 gal)	In excess of 2271 L (600 gal)	
Outdoors		I	I	I	
In separate building	II	II	II	Not permitted	
In special room	III	III	Not permitted	Not permitted	
Inside buildings, but not in a special room and exposed to other occupancies.	IV	Not permitted	Not permitted	Not permitted	

 ^a 29 CFR 1910.103 and NFPA 50B
 ^b This table does not apply to the storage in dewars of the type generally used in laboratories for experimental

purposes.

The location of LH₂ storage, as determined by the maximum total quantity of LH₂, shall be in the order of preference indicated by Roman numerals with I indicating the most preferred and IV the least preferred location.

Table A3.4 — QD^a requirements for nonpropellant LH₂ systems for outdoor locations^{b, c}

Table A3.4 — QD Tequirements for nonpropellant Ln ₂ systems for c			
	Total liquid		•
h		pacity (gal)	
Type of outdoor exposure ^h	39.65	3,501	15,001
	to	to	to
	3,500	15,000	75,000
Building/structure			
 a) Wall(s) adjacent to system constructed of noncombustible 			
materials or limited combustible materials.			
(1) Sprinklered building/structure or unsprinklered			.,
building/structure having noncombustible contents.	5 ^{d,f}	5 ^{d,f}	5 d,f
(2) Unsprinklered building/structure with combustible contents.			
Adjacent wall(s) with fire resistance rating less than 3 hr. e	25	50	75
Adjacent wall(s) with fire resistance rating of 3 hr or greater. ^e	5	5	5
b) Wall(s) adjacent to system constructed of combustible materials			
(1) Sprinklered building/structure	50	50	50
(2) Unsprinklered building/structure	50	75	100
2. Wall openings			
a) Openable	75	75	75
b) Unopenable	25	50	50
3. Air compressor intakes, inlets for air conditioning or ventilating			
equipment.	75	75	75
4. All classes of flammable and combustible liquids (above ground and			_
vent or fill openings if below ground).	50 ⁹	75 ⁹	100 ^g
Between stationary liquefied hydrogen containers	5	5	5
Flammable gas storage (other than hydrogen)	50	75	75
7. Liquid oxygen storage and other oxidizers	75	75	75
Combustible solids	50	75	100
Open flames and welding	50	50	50
10. Places of public assembly	75	75	75
11. Public ways, railroads, and property lines	25	50	75
12. Inlet to underground sewers	5	5	5
13. Protective structures	5 [†]	5 [†]	5 [†]
a D:		•	

Distances are given in units of feet.

b NFPA 50B

The distances in exposure types 1, 4, 6, 7, 8, and 11 shall be permitted to be reduced by two thirds, but not less than 5 ft (1.5 m), for insulated portions of the system; and, for uninsulated portions of the system, by the use of protective structures having a minimum fire resistance rating of 2 h, which interrupts the line of sight between the uninsulated portions of the LH₂ system and the exposure. The protective structure, or the insulated LH₂ tank, shall interrupt the line of sight between uninsulated portions of the LH₂ storage system and the exposure.

d Portions of wall less than 10 ft (3 m) (measured horizontally) from any part of a system shall have a fire resistance rating of at least one-half hour.

Exclusive of windows and doors

Where protective structures are provided, ventilation and confinement of product shall be considered. The 5 ft (1.5 m) distance in exposure types 1 and 13 facilitates maintenance and enhances ventilation.

Distances may be reduced to 15 ft (4.6 m) for Class IIIB combustible liquids (liquids having a flash point at or above 366.5 K (200 °F).

Unloading connections on delivery equipment shall not be positioned closer to any of the exposures cited than the distances given for the storage system.

A.4 Venting and Flow of Hydrogen

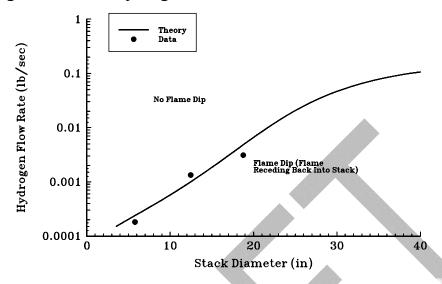
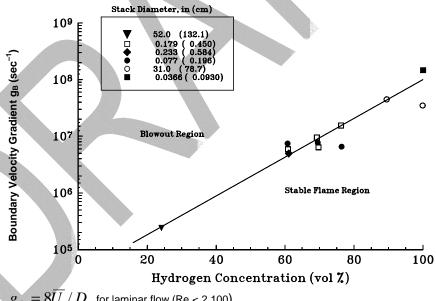


Figure A4.1 — Flame dip as a function of stack diameter and hydrogen flow (Grumer, Strasser, Singer, Gussey, and Rowe 1970)



 $g_{_B}=8\overline{U}~/D$, for laminar flow (Re < 2,100) $g_{_B}=0.0395\overline{U}~{
m Re}^{0.75}/D$, for turbulent flow (Re > 2,100) $^{^{*}}$

 ${}^*\overline{U}$ is the average linear velocity in ft/sec, ${\it D}$ is the diameter in feet, and Re is the Reynolds number based upon these parameters.

Figure A4.2 — Blowout and stable flame region (Grumer, Strasser, Singer, Gussey, and Rowe 1970)

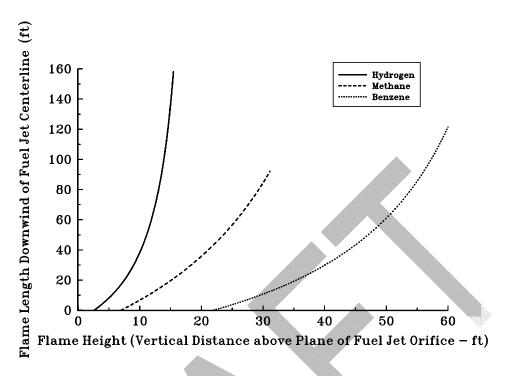


Figure A4.3 — Flame shape in crosswinds (Brzustowski, Gollahalli, and Sullivan 1975; Ordin and Carter 1980)

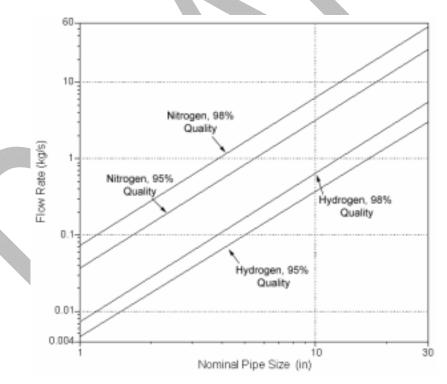


Figure A4.4 — Minimum flow rate for nonstratified, two-phase hydrogen and nitrogen flow for pipeline fluid qualities below 95% and 98%. Liquid and gas phases are assumed to be saturated at the normal boiling point (Liebenberg, Novak, and Edeskuty 1967; Novak 1970).

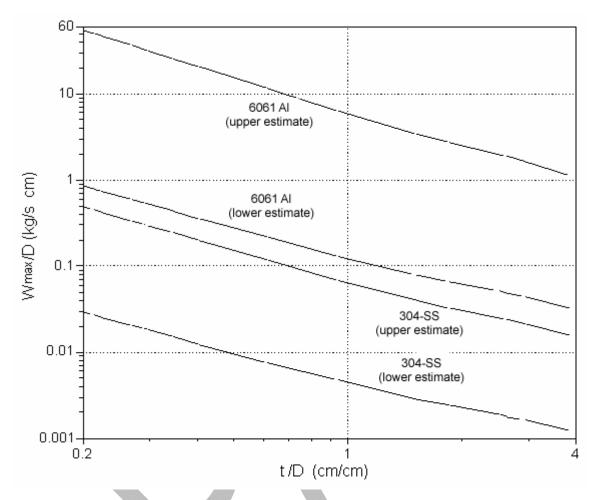


Figure A4.5 — Liquid hydrogen flow rate limits to avoid excessive cooldown stresses in thick-wall piping sections such as flanges for 304 SS and 6061 Al. Upper and lower estimates represent difference in variables such as heat transfer correlation and limiting stress values (Novak 1970). t = maximum radial thickness of flange wall (cm)
d = inside diameter of flange (cm)
W_{max} = cooldown flow rate limit (kg/s)

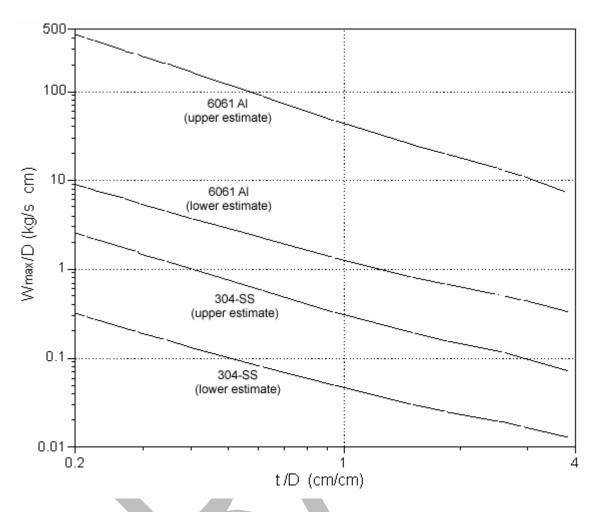


Figure A4.6 — Liquid nitrogen flow rate limits to avoid excessive cooldown stresses in thick-wall piping sections such as flanges for 304 SS and 6061 Al. Upper and lower estimates represent difference in variables such as heat transfer correlation and limiting stress values (Novak 1970).

t = maximum radial thickness of flange wall (cm)

d = inside diameter of flange (cm)

W_{max} = cooldown flow rate limit (kg/s)

Table A4.1 — Summary of liquefied hydrogen spill data

Size of spill (gal)	Surface	Vaporization ^d	Dispersal	Ignition	Radiation
0.18 ^a	Paraffin wax	Yes	No	No	No
1.8 ^a	Macadam	No	Visible cloud rise only	No	No
1.8 ^a	Gravel	No	Visible cloud rise only	No	No
14.4 ^a	Gravel	No	No	Yes	Flame size only
15.4 ^a	Steel	No	No	Yes	Flame size only
.8 ^a	Macadam	No	Vertical concentrations in quiescent atmosphere	No	No
2.0-23.6 ^a	Gravel	No	No	Yes	Flame size and radiant heat flux
23.5-44.4 ^b	Sand	Yes	No	No	No
35.2 ^b	Bank Gravel	Yes	No	No	No
25-50 ^b	Crushed rock	Yes	No	No	No
1.3 ^b	Sand	Yes	Observations of visible vaporization time cloud	Yes	Fireball size only
32 ^b	Sand	Yes	Observations of visible	No	Fireball size only
			vaporization time cloud		
500 b	Sand	Yes	Observations of visible vaporization time cloud	No	Fireball size and radiant heat flux
5,000 b	Sand	No	No	Yes ^c	Fireball size and radiant heat flux

^a Zebatakis and Burgess 1961
^b A. D. Little 1960
^c Inadvertently
^d Listing indicates whether the amount of vaporization was determined.

A.5 Materials

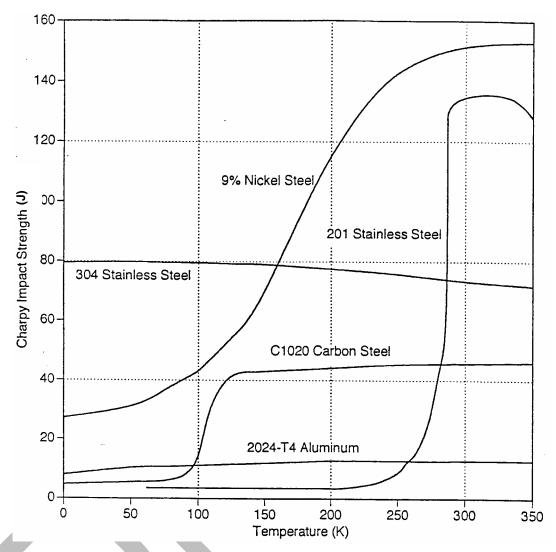


Figure A5.1 — Charpy impact strength as a function of temperature for various materials (Brown, Mindlin, and Ho 1996; Durham, McClintock, and Reed 1962)

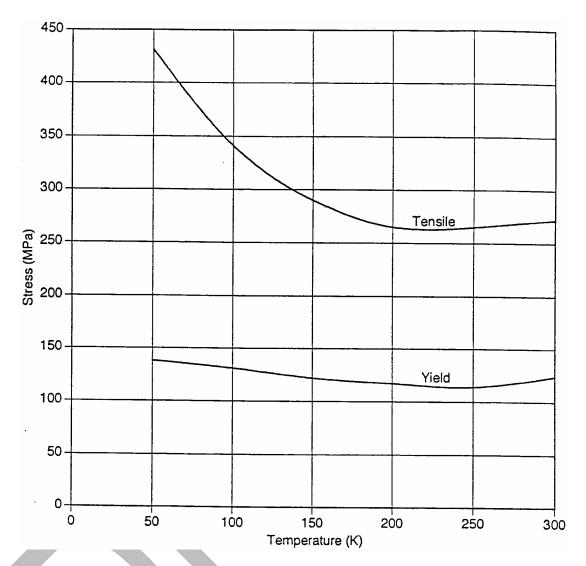


Figure A5.2 — Yield and tensile stress of 5086 Al as a function of temperature (McClintock and Gibbons 1960)

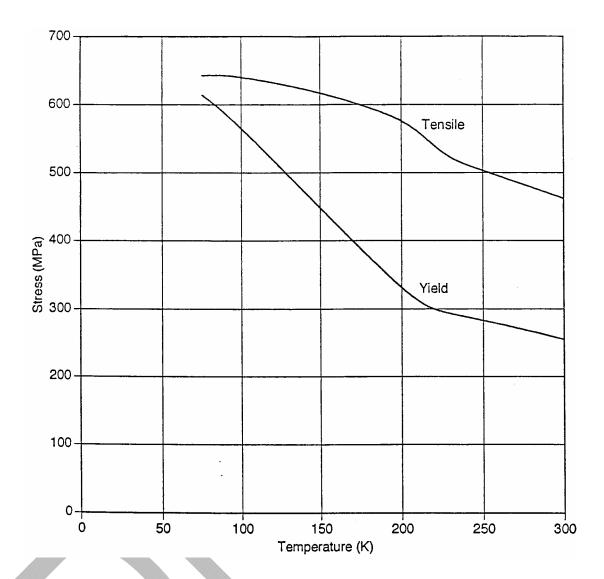


Figure A5.3 — Yield and tensile stress of AISI 430 stainless steel as a function of temperature (McClintock and Gibbons 1960)

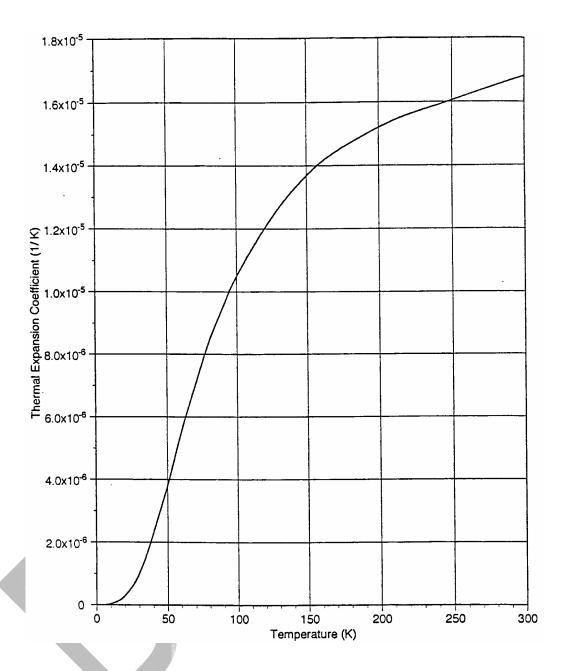


Figure A5.4 — Thermal expansion coefficient of copper as a function of temperature (Johnson 1960)

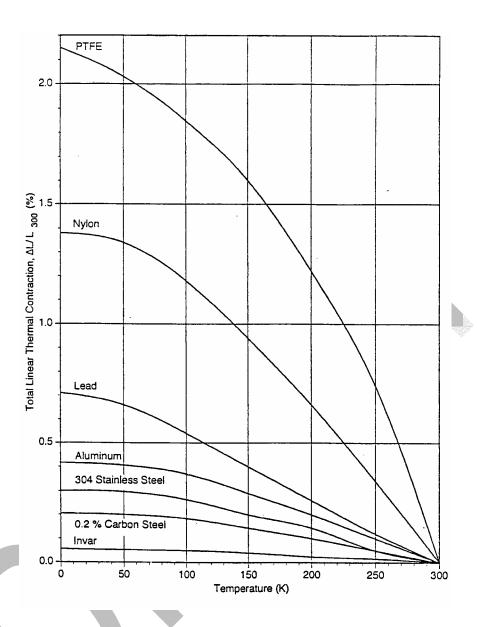


Figure A5.5 — Total linear thermal contraction as a function of temperature for several materials showing the total contraction at a given temperature as the temperature is lowered from 300 K (80 °F) to the lower temperature. PTFE = Polytetrafluoroethylene (Teflon™) (Wigley and Halford 1971)

Table A5.1 — Summary of material compatibility for hydrogen service

Table A5.1 — Summary of material compatibility for hydrogen service							
Material		Service		Remarks			
water lai	GH ₂	LH ₂	SLH ₂	itellia ks			
Aluminum and its alloys	Yes	Yes	Yes				
Austenitic stainless steels with > 7% nickel	Yes	Yes	Yes	Some make martensitic conversion			
(such as, 304, 304L, 308, 316, 321, 347)				if stressed above yield point at low temperature.			
Carbon steels	Yes	No	No	Too brittle for cryogenic service			
Copper and its alloys (such as, brass,	Yes	Yes	Yes				
bronze, and copper-nickel)							
Gray, ductile, or cast iron	No	No	No	Not permitted for hydrogen service			
Low-alloy steels	Yes	No	No	Too brittle for cryogenic service			
Nickel and its alloys	No	Yes	Yes	Susceptible to hydrogen			
(such as, Inconel™ and Monel™ or the				embrittlement			
equivalent)							
Nickel steels (such as, 2.25, 3.5, 5, and	No	No	No	Ductility lost at LH ₂ and SLH ₂			
9% Ni)				temperatures			
Titanium and its alloys	No	Yes	Yes	Susceptible to hydrogen			
				embrittlement.			
Chloroprene rubber (neoprene)	Yes	No	No	Too brittle for cryogenic service			
Dacron [™] (or the equivalent)	Yes	No	No	Too brittle for cryogenic service			
Fluorocarbon rubber (Viton™ or the	Yes	No	No	Too brittle for cryogenic service			
equivalent)							
Mylar (or the equivalent)	Yes	No	No	Too brittle for cryogenic service			
Nitrile (buna-n)	Yes	No	No	Too brittle for cryogenic service			
Polyamides (nylon)	Yes	No	No	Too brittle for cryogenic service			
Polychlorotrifluorethylene (PCTFE)	Yes	Yes	Yes	*			
Polytetrafluorethylene (Teflon™ or the	Yes	Yes	Yes				
equivalent)							

Table A5.2 — A selection of recommended materials for typical applications

Application	Typical materials recommended				
	LH ₂ or SLH ₂	GH₂			
Valves	Forged, machined, and cast valve bodies (304 or 316 stainless steel, or brass) with extended bonnet, and with other materials inside	Appropriate industrial products ^a			
Fittings	Stainless steel bayonet type for vacuum jackets ^b	Appropriate industrial products ^a			
O-rings	Stainless steel ^c , PCTFE, or Teflon™*	Appropriate industrial products ^a			
Gaskets	Soft Aluminum, lead, or annealed copper between serratedflanges; PCTFE; Teflon™; glass-filled Teflon™	Appropriate industrial products ^a			
Flexible hoses	Convoluted vacuum jacketed 316 or 321 stainless steel	Stainless steel braided with Teflon™- lining			
Rupture disk assembly	304, 304L, 316, or 316L stainless steel	304, 304L, 316, or 316L stainless steel			
Piping	304, 304L, 316, or 316L stainless steel	300 series stainless steel (316 preferred ^d) Carbon steel ^e			
Dewars	304, 304L, 316, or 316L stainless steel	Not applicable			
Lubricants	No lubricants used in some applications. d Lubricants listed for GH₂ are compatible but will become solid at low temperatures. Dry lubricants, such as PTFE, PTFE carbon, PTFE bronze, fiberglass-PFTE graphite. Graphite and molybdenum disulfide permit only very limited service life for bearings. 9	Dupont Krytox [™] 240AC, Fluoramics OXY-8, Dow Corning DC-33, Dow Corning FS-3452, Bray Oil Braycote [™] 601, General Electric Versilube [™] , Houghton Cosmolube 5100, Braycote [™] 640 AC, Dupont GPL 206, Halocarbon Series 6.3 oil, and PCTFE oil*			

or the equivalent

A number of standard industrial products are available, covering a wide range of temperatures and

pressures in a variety of compatible materials.

Threaded joints should be avoided in LH₂ or SLH₂ systems. If they must be used, the male and female threads should be tinned with a 60% lead/40% tin solder, then heated to provide a soldered joint with pipe thread strength.

Metal O-rings have proven satisfactory when coated with a soft material and when used on smooth surfaces. Type 321 stainless steel, with a coating of Teflon™ or silver, should be used in stainless steel flanges with stainless bolting. Teflon™-coated aluminum should be used in aluminum flanges with aluminum bolting. Using similar materials avoids the leakage possibility from unequal contraction of dissimilar metals.

McPherson, B., private communication 1996

Carbon steel meeting ASME B31.3 standards may be used for GH₂ service above 244 K (-20 °F)

Peschka 1992

Wigley 1971

Table A5.3 — Minimum temperatures and basic allowable stresses in tension for selected metals^a

Metal and/or alloy ^b	Metal form ^c	Minimum temperature ^d K (°F)	Specified minimum tensile strength MPa (ksi)	Specified minimum yield strength MPa (ksi)	Basic allowable stres MPa (ksi)
	T	Aluminum a			T
NP1100-0, B361	forging & fitting	4.2 (-452)	75.8 (11)	20.7 (3)	13.8 (2.0)
1100-0, B241	pipe & tube	4.2 (-452)	75.8 (11)	20.7 (3)	13.8 (2.0)
3003-0, B241	pipe & tube	4.2 (-452)	96.5 (14)	34.5 (5)	22.8 (3.3)
5083-0, B209	plate & sheet	4.2 (-452)	275.8 (40)	124.1 (18)	82.7 (12.0)
5083-0, B241 WP6061-T6, B361	pipe & tube forging & fitting	4.2 (-452) 4.2 (-452)	268.9 (39) 262.0 (38)	110.3 (16) 241.3 (35)	73.8 (10.7)
6061-T6, B241	pipe & tube	4.2 (-452)	262.0 (38)	241.3 (35)	87.6 (12.7) 87.6 (12.7)
0001 10, B2+1	pipe a tube	Copper & copper		241.5 (00)	07.0 (12.7)
Cu Forging, B283	forging	4.2 (-452)	227.5 (33)	75.8 (11)	50.3 (6.7)
Cu Plate, B152	plate & sheet	4.2 (-452)	206.8 (30)	68.9 (10)	46.2 (5.8)
Cu Pipe, B42, annealed	pipe & tube	4.2 (-452)	206.8 (30)	62.1 (9)	41.4 (6.0)
Red brass pipe	pipe & tube	4.2 (-452)	275.8 (40)	82.7 (12)	55.2 (8.0)
0Cu-10Ni, B171	plate & sheet	4.2 (-452)	275.8 (40)	103.4 (15)	68.9 (10.0)
0Cu-10Ni, B466	pipe & tube	4.2 (-452)	262.0 (38)	89.6 (13)	60.0 (8.4)
'0Cu-30Ni, B171	plate & sheet	4.2 (-452)	482.6 (70)	206.8 (30)	137.9 (20.0)
0Cu-30Ni, B466	pipe & tube	4.2 (-452)	344.7 (50)	124.1 (18)	82.7 (12.0)
l' D000		Nickel & nickel		00 = ((0)	FF 2 (2.5)
li, B366	forging & fitting	74.8 (-325)	379.2 (55)	82.7 (12)	55.2 (8.0)
li, B162	plate & sheet	74.8 (-325)	379.2 (55)	103.4 (15)	68.9 (10.0)
li, B161	pipe & tube	74.8 (-325) 74.8 (-325)	379.2 (55) 482.6 (70)	103.4 (15)	68.9 (10.0)
li-Cu, B564 li-Cu, B127	forging & fitting plate & sheet	74.8 (-325) 74.8 (-325)	482.6 (70)	172.4 (25) 193.1 (28)	115.1 (16.7) 128.9 (18.7)
li-Cu, B127	pipe & tube	74.8 (-325)	482.6 (70)	193.1 (28)	128.9 (18.7)
li-Cr-Fe, B564	forging & fitting	74.8 (-325)	551.6 (80)	241.3 (35)	160.6 (23.3)
li-Cr-Fe, B168	plate & sheet	74.8 (-325)	551.6 (80)	241.3 (35)	160.6 (23.3)
li-Cr-Fe, B167	pipe & tube	74.8 (-325)	551.6 (80)	206.8 (30)	137.9 (20.0)
	F-F	Steel, carbo			10110 (=010)
285 Grade C,	plate & sheet	1	379.2 (55)	206.8 (30)	126.2 (18.3)
285 Grade C, A524	pipe & tube	244 (-20)	379.2 (55)	206.8 (30)	126.2 (18.3)
442 Grade 50, A672	pipe & tube		413.7 (60)	220.6 (32)	137.9 (20.0)
	400000	Steel, low & interme		,	
.5 Ni, A420	forging & fitting	172 (-150)	448.2 (65)	241.3 (35)	149.6 (21.7)
5.5 Ni, A203	plate	244 (-20)	448.2 (65)	255.1 (37)	149.6 (21.7)
5.5 Ni, A333	pipe & tube	172 (-150)	448.2 (65)	241.3 (35)	149.6 (21.7)
Ni, A645	plate	103 (-275)	655.0 (95)	448.2 (65)	218.6 (31.7)
Ni, A420 Ni, A353	forging & fitting	77 (-320)	758.4 (110)	517.1 (75)	218.6 (31.7) 218.6 (31.7)
Ni, A333	plate pipe & tube	77 (-320) 77 (-320)	689.5 (100) 689.5 (100)	517.1 (75) 517.1 (75)	218.6 (31.7)
NI, A333	pipe & tube	Steel, stainless,		317.1 (73)	210.0 (31.7)
05 (12Cr-Al), A240	plate & sheet	244 (-20)	413.7 (60)	172.4 (25)	115.1 (16.7)
30 (17Cr), A240	plate & sheet	244 (-20)	448.2 (65)	206.8 (30)	137.9 (18.4)
00 (11 0.), 1.12 10	plate d'eller	Steel, stainless, m		200.0 (00)	107.10 (101.1)
10 (13Cr), A240	plate & sheet	244 (-20)	448.2 (65)	206.8 (30)	126.9 (18.4)
		Steel, stainless, a	ustenitic	, ,	. , ,
04 (18Cr-8Ni)	plate & sheet	19.3 (-425)	517.1 (75)	206.8 (30)	137.9 (20.0)
04	pipe & tube	19.3 (-425)	517.1 (75)	206.8 (30)	137.9 (20.0)
304 (18Cr-8Ni)	forging & fitting	19.3 (-425)	517.1 (75)	206.8 (30)	137.9 (20.0)
04L (18Cr-8Ni)	plate & sheet	19.3 (-425)	482.6 (70)	172.4 (25)	115.1 (16.7)
04L	pipe & tube	19.3 (-425)	482.6 (70)	172.4 (25)	115.1 (16.7)
304L (18Cr-8Ni)	forging & fitting	19.3 (-425)	482.6 (70)	172.4 (25)	115.1 (16.7)
10 (25Cr-20Ni)	plate & sheet	74.8 (-325)	517.1 (75)	206.8 (30)	137.9 (20.0)
310 (25Cr-20Ni)	forging & fitting	74.8 (-325)	517.1 (75)	206.8 (30)	137.9 (20.0)
10S (25Cr-20Ni) 10S	plate & sheet	74.8 (-325)	517.1 (75)	206.8 (30)	137.9 (20.0)
16 (16Cr-12Ni-2Mo)	pipe & tube plate & sheet	74.8 (-325) 19.3 (-425)	517.1 (75) 517.1 (75)	206.8 (30) 206.8 (30)	137.9 (20.0) 137.9 (20.0)
16 (16C1-12N1-2NIO)	piate & sneet	19.3 (-425)	517.1 (75)	206.8 (30)	137.9 (20.0)
316 (16Cr-12Ni-2Mo)	forging & fitting	74.8 (-325)	517.1 (75)	206.8 (30)	137.9 (20.0)
16L (16Cr-12Ni-2Mo)	plate & sheet	19.3 (-425)	482.6 (70)	172.4 (25)	115.1 (16.7)
16L	pipe & tube	74.8 (-325)	482.6 (70)	172.4 (25)	115.1 (16.7)
316L (16Cr-12Ni-2Mo)	forging & fitting	19.3 (-425)	482.6 (70)	172.4 (25)	115.1 (16.7)
21 (18Cr-10Ni-Ti)	plate & sheet	74.8 (-325)	517.1 (75)	206.8 (30)	137.9 (20.0)
21 (18Cr-10Ni-Ti)	pipe & tube	74.8 (-325)	517.1 (75)	206.8 (30)	137.9 (20.0)
321 (18Cr-10Ni-Ti)	forging & fitting	74.8 (-325)	517.1 (75)	206.8 (30)	137.9 (20.0)
47 (18Cr-10Ni-Cb)	plate & sheet	19.3 (-425)	517.1 (75)	206.8 (30)	137.9 (20.0)
			517.1 (75)	206.8 (30)	137.9 (20.0)
347	pipe & tube	19.3 (-425)	317.1 (73)	200.0 (30)	137.9 (20.0)

Table A5.3 — Minimum temperatures and basic allowable stresses in tension for selected metals^a (continued)

Titanium & titanium alloy					
Ti, B337	pipe & tube	214 (-75)	241.3 (35)	172.4 (25)	80.7 (11.7)
Ti-0.2Pd, B337	pipe & tube	214 (-75)	344.7 (50)	275.8 (40)	115.1 (16.7)

^a ASME B31.3

ASME B31.3 should be consulted for special notes regarding restrictions on this material.

Table A5.4 — Elastic properties of selected materials at room temperature and liquid hydrogen temperature

	on temperature and liquid riyurogen temperature					
Temperature	_			Poisson's		
•				Ratio		
()	(GPa)	(GPa)	(GPa)	Hallo		
Aluminum		7				
300	TBA ^d	TBA	TBA	TBA		
20	TBA	TBA	TBA	TBA		
300	71.6 ^a	26.82 ^a	71.56 ^a	0.3334 ^a		
20	80.8 ^a	30.68 ^a	74.23 ^a	0.3184 ^a		
300		26.36 ^a	72.14 ^a	0.3383 ^a		
20	77.7 ^a	29.22 ^a	74.8 ^a	0.3269 ^a		
Invar [⊤]	M*					
300	152.5 ^a	55.8 ^a	110.9 ^a	0.2843 ^a		
20	141.5 ^a	50.5 ^a	124.1 ^a	0.3183 ^a		
Stainless	steels					
300	189.8 ^a	73.5 ^a	150.7 ^a	0.2901 ^a		
20	204.5 ^a	80.4 ^a	148.8 ^a	0.2714 ^a		
300	TBA	TBA	TBA	TBA		
20	TBA	TBA	TBA	TBA		
300	183.7 ^a	70.2 ^a	159.2 ^a	0.3074 ^a		
20	198.8 ^a	76.7 ^a	162.3 ^a	0.2958 ^a		
300	203.8 ^a	78.5 ^a	167.7 ^a	0.2972 ^a		
20	220.6 ^a	86.0 ^a	168.4 ^a	0.2819 ^a		
Fluorocarbon resins						
300	0.55 b,c	TBA	TBA	TBA		
20	4.27 b,c	TBA	TBA	TBA		
300	0.48 b,c	TBA	TBA	TBA		
20	5.03 b,c	TBA	TBA	TBA		
	Temperature (K) Aluminum 300 20 300 20 300 20 Invar¹ 300 20 Stainless 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300 20 300	Temperature (K) Young's Modulus (GPa) Aluminum alloys 300 TBA ^d 20 TBA TBA 300 71.6a 70.2a 20 77.7a 152.5a 20 141.5a 152.5a 20 141.5a 189.8a 20 204.5a 300 300 183.7a 20 20 198.8a 300 20 198.8a 20 20 20.6a Fluorocarbon resins 300 0.55 b,c 20 20 4.27 b,c 300 300 0.48 b,c	Temperature (K) Young's Modulus (GPa) Shear Modulus (GPa) Aluminum alloys 300 TBAd TBA TBA TBA 20 80.8a 30.68a 30.6	Temperature (K) Young's Modulus (GPa) Shear Modulus (GPa) Bulk Modulus (GPa) Aluminum alloys 300 TBAd TBA		

or the equivalent

^o ASME B31.3 should be consulted regarding grade and specifications for this material.

The minimum temperature shown is that design minimum temperature for which the material is normally suitable without impact testing other than that required by the material specification. However, the use of a material at a design minimum temperature below 244 K (-20 °F) is established by rules in ASME B31.3, including any necessary impact test requirements.

Basic allowable stress in tension for the temperature range from the minimum temperature to 311 K (100 °F)

f ASME B31.3 should be consulted regarding the minimum temperature for this material.

^a D. Mann 1977

b Unfilled resin

E. I. du Pont de Nemours and Co. 1976

TBA = to be added

Table A5.5 — Mechanical properties of selected materials at room temperature and liquid hydrogen temperature

temperature									
Material	Temperature (K)	Yield Strength (MPa)	Tensile Strength (MPa)	Axial Fatigue Strength ^a (MPa)					
	Aluminum Alloys								
3003-0	300	40 ^c	110 ^c						
	20	69 ^c	375 ^c						
5083-0	300	141 ^c	310°	235 ^{c,g}					
	20	170 ^c	520°	283 ^{c,h}					
6061-T6	300	278 ^c	310°	200 ^c					
	20	350°	498 ^c	383 ^c					
Invar™*									
	300	280 ^{c,i}	510 ^{c,i}						
	20	780 ^{c,i}	1040 ^{c,i}						
	Stainless								
304	300	276 ^{c,l}	640 ^{c,i}	190 ^{c,j}					
	20	393 ^{c,l}	1730 ^{c,i}						
304L	300	280 ^{c,l}	600 ^{c,i}	210 ^{c,t}					
	20	380 ^{c,l}	1730 ^{c,i}	210 ^{b,c,f}					
310	300	200 ^{c,k}	550 ^{c,i}	280 ^c					
	20	680 ^{c,k}	1260 ^{c,i}	520 ^{b,c}					
316	300	230 ^{c,i}	570°						
	20	610 ^{c,i}	1400 ^c						
Fluorocarbon Resins									
Polytetrafluorethylene	300	11.7 ^{d,e}	31.0 ^{d,e}						
(Teflon™*) (PTFE or TFE)	20	122.7 d,e	123.4 ^{d,e}						
Polytetrafluorethylene	300	13.8 ^{d,e}	27.6 ^{d,e}						
copolymer	20	163.4 ^{d,e}	164.1 ^{d,e}						
Hexafluoropropylene (FEP)									

or the equivalent

Axial fatigue strength at fatigue life of 10⁶ cycles At 77 K, not 20 K
Mann 1977.
Unfilled resin

E. I. du Pont de Nemours and Co. 1976

Triaxial

H321 Temper, 295 K H32 Temper, 77 K

Annealed

Annealed, Uniaxial, 295 K Annealed, Bar Annealed, Plate and Bar

Table A5.6 — Thermal properties of selected materials at room temperature and liquid hydrogen temperature

Material	Temperature (K)	CONGLICTIVITY NEXT		Instantaneous thermal expansion ^a (1/K)	Linear thermal expansion ^b (m/m)					
Aluminum alloys										
3003	300	175 ^d	902 ^{d,f}	23.2 x 10 ^{-6 d,f}	+16 x 10 ^{-5 d,f}					
	20	58 ^d	8.9 ^{d,f}	0.2 x 10 ^{-6 d,f}	-415 x 10 ^{-5 d,f}					
5083	300	118 ^d	902 ^{d,f}	23.2 x 10 ^{-6 d,f}	+16 x 10 ^{-5 d,f}					
	20	17.2 ^d	8.9 ^{d,f}	0.2 x 10 ^{-6 d,ff}	-415 x 10 ^{-5 d,f}					
6061	300	NA	902 ^{d,f}	23.2 x 10 ^{-6 d,f}	+16 x 10 ^{-5 d,f}					
	20	NA	8.9 ^{d,f}	0.2 x 10 ^{-6 d,f}	-415 x 10 ^{-5 d,f}					
	•	Invar™*								
	300	14 ^d	NA	1.2 x 10 ^{-6 d}	O_q					
	20	1.65 ^d	11.8 ^d	0_q	-40 x 10 ^{-5 d}					
	Stai	nless steels								
304	300	14.7 ^d	NA	15.9 x 10 ^{-6 d}	+12 x 10 ^{-5 d}					
	20	2.12 ^d	12.7 ^d	0.7 x 10 ^{-6 d}	-298 x 10 ^{-5 d}					
304L	300	14.7 ^d	NA	15.9 x 10 ^{-6 d}	+12 x 10 ^{-5 d}					
	20	2.12 ^d	11.8 ^d	0.5 x 10 ^{-6 d}	-298 x 10 ^{-5 d}					
310	300	11.5 ^d	475 ^d	15.9 x 10 ^{-6 d}	+12 x 10 ^{-5 d}					
	20	1.71 ^d	11.6 ^d	0.5 x 10 ^{-6 d}	-298 x 10 ^{-5 d}					
316	300	14.7 ^d	480 ^d	15.9 x 10 ^{-6 d}	+12 x 10 ^{-5 d}					
	20	2.12 ^d	13.7 ^d	0.5 x 10 ^{-6 d}	-298 x 10 ^{-5 d}					
	Fluoro	carbon resins								
Polytetrafluorethylene (Teflon™*)	300	0.25 ^h	1,010 ^{c,f}	1.5 x 10 ^{-4 e,g}	O ⁱ					
(PTFE or TFE)	20	0.13 ^h	76 ^f	NA	-2,150 x 10 ^{-5 i}					
Polytetrafluorethylene copolymer	300	0.20 ^h	1,088 ^h	* TBA ^j	O ⁱ					
hexafluoropropylene (FEP)	20	0.12 ^h	TBA	TBA	-1,800 x 10 ^{-5 i}					

or the equivalent

mann 1977

at 295 K, not 300 K

Johnson 1960

Reed, Schramm, and Clark 1973

Cadillac Plastic and Chemical Co. 1980

Schwartzberg, Osgood, and Herzog 1968

TBA = to be added

___Table A5.7 — Typical characteristics of hydrogen embrittlement types^a

Characteristic	Environmental hydrogen embrittlement	Internal hydrogen embrittlement	Hydrogen reaction embrittlement
Usual source of hydrogen	Gaseous hydrogen	Processing, electrolysis, corrosion	Gaseous or atomic hydrogen from any source.
Typical conditions	10 ⁻⁶ to 10 ⁸ Pa H ₂ gas pressure. Most severe near room temperature. Observed from -100 to 700 °C. Gas purity and strain rate important.	0.1 to 10 ppm average H ₂ content. Most severe near room temperature. Observed from -100 to 100 °C. Strain rate is important.	Heat treatment or service in H ₂ , especially at elevated temperatures.
Test methods for embrittlement	Notched tensile; unnotched tensile, creep rupture; fatigue (low, high cycle); fracture toughness; disk pressure test.	Notched tensile delayed failure; slow strain rate tensile; bend tests; C-rings; torqued bolts.	Visual or metallographic observation.
Location of crack initiation	On surface or internal.b	Internal crack initiation; incubation (reversible); slow discontinuous growth; and fast fracture.	Usually internal initiation from bubbles or flakes.
Rate- controlling embrittlement step	Adsorption is transfer step; absorption or lattice diffusion ^b is embrittling step.	Lattice diffusion to internal stress risers.	Chemical reaction to form hydrides or gas bubbles.
^a Gray 1974 ^b Unresolved			

Table A5.8 — Susceptibility of materials to embrittlement in hydrogen at 10,000 psi and 72 °Fa

Table A5.8 — Susceptibil			Unnotched ductility			
Material	Strength	ratio, H₂/He		gation %	Reduction	on of Area %
	Notched ^b	Unnotched	He	H ₂	He	H ₂
		Extremely embri	ttled			
18Ni-250 Maraging Steel	0.12	0.68	8.2	0.2	55	2.5
410 Stainless Steel	0.22	0.70	15	1.3	60	12
1042 Steel (quenched and tempered)	0.22					
17-7 PH Stainless Steel	0.23	0.92	17	1.7	45	2.5
Fe-9Ni-4Co-0.20C	0.24	0.86	15	0.5	67	15
H-11	0.25	0.57	8.8	0	30	0
René 41	0.27	0.84	21	4.3	29	11
Electro-Formed Nickel	0.31					
4140	0.40	0.96	14	2.6	48	9
Inconel™ 718*	0.46	0.93	17	1.5	26	1
440C	0.50	0.40	4		3.2	0
		Severely embrit	tled			
Ti-6A1-4V (STA)	0.58		7			
430F	0.68		22	14	64	37
Nickel 270	0.70		56	52	89	67
A515	0.73		42	29	67	35
HY-100	0.73		20	18	76	63
A372 (class IV)	0.74		20	10	53	18
1042 (normalized)	0.75				59	27
A533-B	0.78				66	33
Ti-6A1-4V (annealed)	0.79					
AISI 1020	0.79	A			68	45
HY-50	0.80				70	60
Ti-5A1-2.5Sn (ELI)	0.81				45	39
Armco Iron	0.86				83	50
		Slightly embritt	ed			
304 ELC Stainless Steel	0.87				78	71
305 Stainless Steel	0.89				78	75
Be-Cu Alloy 25	0.93				72	71
Titanium	0.95				61	61
		Negligibly embri	ttled			
310 Stainless Steel	0.93	P			64	62
A286	0.97				44	43
7075-T73 Aluminum Alloy	0.98				37	35
316 Stainless Steel	1.00				72	75
OFHC Copper	1.00				94	94
NARloy-Z ^c	1.10				24	22
6061-T6 Aluminum Alloy	1.10				61	66
1100 aluminum	1.40				93	93
NOTE: Dashes indicate no	information o	woilabla				

NOTE: Dashes indicate no information available.

^{*} or the equivalent

Chandler and Walter 1974

Stress concentration factor, K_t, = 8.4

Tested in 7,000 psi (48.3 MPa) hydrogen

alloys	Test			ngth si)	Ductility					
Alloy	Environment	Test pressure (psi)	Yield	Ultimate	Reduction in area (%)	Elongation (%)				
Aluminum alloys										
2011	Air	14.5	39.0 x 10 ³	49.1 x 10 ³	48	17				
	He	10,000	32.9 x 10 ³	42.9 x 10 ³	57	18				
	H ₂	10,000	31.9 x 10 ³	42.9 x 10 ³	58	17				
2024	Air	14.5	51.9 x 10 ³	70.9 x 10 ³	33	15				
	He	10,000	46.9 x 10 ³	63.9 x 10 ³	36	19				
	H ₂	10,000	44.9 x 10 ³	61.9×10^3	35	18				
6061	Air	14.5	25.9 x 10 ³	33.9×10^3	75	14				
	He	10,000	28.9 x 10 ³	25.9 x 10 ³	82	15				
	H ₂	10,000	20.0 x 10 ³	26.9 x 10 ³	82	14				
6063	Air	14.5	31.0 x 10 ³	34.9 x 10 ³	62	13				
	He	10,000	22.9 x 10 ³	27.9 x 10 ³	83	15				
	H ₂	10,000	22.9 x 10 ³	29.0 x 10 ³	84	15				
	2	Nickel and	I nickel alloys	4337						
Nickel	He	10,000	26.0×10^3	61.9×10^3	79	57				
	H ₂	10,000	24.9 x 10 ³	62.9 x 10 ³	54	47				
Inconel™	He	10,000	151 x 10 ³	186 x 10 ³	40	25				
718*	H ₂	10,000	155 x 10 ³	186 x 10 ³	11	9				
Inconel™	Air	14.7	152 x 10 ³	204 x 10 ³	45	21				
700*	He	10,000	149 x 10 ³	195 x 10 ³	44	22				
	H ₂	10,000	149 x 10 ³	177 x 10 ³	14	10				
Hastelloy™ X*	Air	14.7	46.9 x 10 ³	99.9 x 10 ³	69	56				
	He	10,000	41.0 x 10 ³	99.9 x 10 ³	68	59				
	H ₂	10,000	41.9 x 10 ³	94.9 x 10 ³	58	55				
	_	Сорр	er alloys							
OFHC	Air	14.7	13.9×10^3	33.9 x 10 ³	71	44				
	H ₂	10,000	13.9x10 ³	33.1 x 10 ³	71	45				
70-30 brass	Air	14.7	17.9 x 10 ³	52.9 x 10 ³	70	59				
	H ₂	10,000	14.9 x 10 ³	50.0 x 10 ³	84	58				
Aluminum	Air	14.7	32.5 x 10 ³	87.0 x 10 ³	67	48				
bronze	H ₂	10,000	30.7 x 10 ³	83.5 x 10 ³	71	49				

or the equivalent

a Chandler and Walter 1975
b Groenvald and Elcea 1974
c Robinson 1977
d Hoover et al. 1980
e Stuhrke and Carpenter 1975

A.6 Hydrogen and Hydrogen Fire Detection

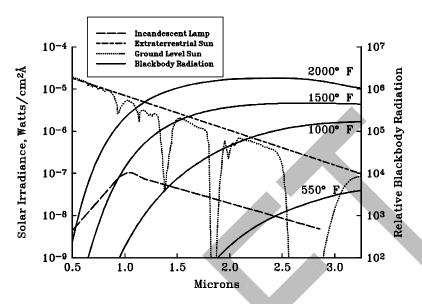


Figure A6.1 — Irradiance of common IR sources (Rosen, Dayan, and Proffitt 1970)

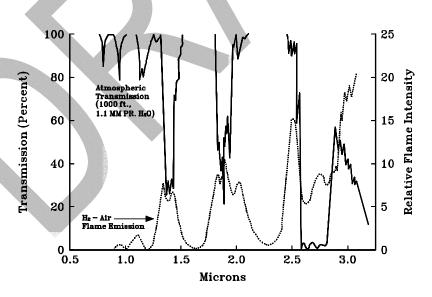


Figure A6.2 — Atmospheric IR transmission and H₂-air-flame emission (Rosen, Dayan, and Proffitt 1970)

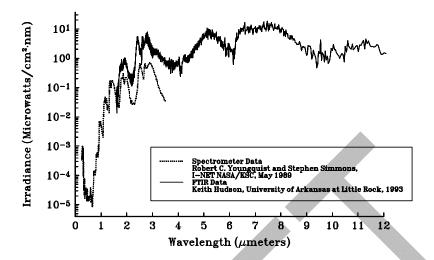


Figure A6.3 — UV/VIS/near-IR emissions (Barnes, H.L., private communication; NASA Stennis Space Center, 1995)

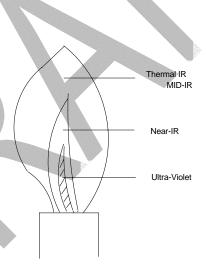


Figure A6.4 — Flame components. Note: A larger portion of the flame emits in the thermal infrared than in the ultraviolet. This means that a fire looks bigger with a thermal imager than it does with a near-infrared imager.

Table A6.1 — Typical hydrogen gas detectors

Table A6.1 — Typical hydrogen Type of detector	Description
Catalytic	A palladium and/or platinum catalyst is used to facilitate the combustion of hydrogen with oxygen. A sensing element detects the heat of combustion.
Electro chemical	Liquid or solid electrolytes surrounding a sensing electrode and a counter electrode. Reaction with hydrogen product produces a current. The hydrogen gas must flow through a gas permeable membrane to reach the electrolyte.
Semi-conducting oxide	Hydrogen gas reacts with chemisorbed oxygen in a semiconductor material, such as tin oxide, and changes the resistance of the material.
Thermal conductivity	The rate of heat conduction from a heat source into the surrounding environment is dependent on the thermal conductivity of that environment.
Mass spectrometer	The gas is ionized and then accelerated through an electric field along a curved path. The amount of curvature induced by the electric field is dependent on the mass of the particle and is used to separate the particles by mass. A detector is placed in the path of the desired gas to be measured.
Sonic	Leaking gas can produce acoustical emissions in the range of 30 to 100 kHz, with 40 kHz being the most common.
Optical	The differences in the refractive index of various gases can be used for detection in sensors using optical interferometry.
Glow plug	Glow plugs are not a true gas detection technique. When a combustible gas mixture exists, the glow plug ignites the mixture and then the fire is detected with heat sensors.

Table A6.2 . Δ survey and analysis of commercially available hydrogen sensors^a

Conditions	con	atalytic nbustic ensors	on	Se	o chen ensors		oxid	conduction conductions	ors	c	al cond letector	rs
	D	RT	PR	D	RT	PR	D	RT	PR	D	RT	PR
293 K/200 ppm	Τ.	0	-		n air					+	0	+
	+	0	-	+	+	+	+	+	+	+	0	+
293 K/2% H ₂	-	-	-	+	+	+	+	+	+	+	0	+
293 K/100% H ₂		?						?	?		?	?
77 K/200 ppm	+	?	-	-	-	-	+	?	?	+	?	?
77 K/2% H ₂	+ -	<u> </u>	_	_	_	_	+	?	?	+	?	?
77 K/100% H ₂		_	_			_			A	T .	<u> </u>	
293 K/200 ppm	-	T -	-	+	nelium +	+	_			l <u>-</u>	-	-
293 K/2% H ₂	-	<u> </u>	-	+	+	+	-		-	-	-	-
	-	-	_	+	+	+	- 4			_	_	-
293 K/100% H ₂ 77 K/200 ppm				-			-	-	-	-		
77 K/200 ppm 77 K/2% H ₂	-	-	-	-	-	-	-	-	-	-	-	-
	-	_		_	_	-4	-	_			-	_
77 K/100% H ₂					itrogen		300					
293 K/200 ppm	T -	-	_	+	+	+	_	-	-	+	0	+
293 K/2% H ₂	-	-	-	+	+	+	-		-	+	0	+
293 K/100% H ₂	-	-	-	+	+	+	-		-	+	0	+
77 K/200 ppm	-	_	_	_	-		-4	-	_	+	?	?
77 K/2% H ₂	-	-	-	-	-	7	Y -	-	-	+	?	?
77 K/100% H ₂	-	-	A	-	-	-	-	-	-	+	?	?
77 10 100 /0 112	ı	1		ln v	acuum					l		
293 K/200 ppm	-	-	-\	1	-	-	-	-	-	+	0	+
293 K/2% H ₂	-	-	-	-	',	j.	- `	-	-	+	0	+
293 K/100% H ₂	-	-	-	-	-	-	-	-	% -	+	0	+
77 K/200 ppm	-	-	-	-	-		-	-	-	+	?	?
77 K/2% H ₂	•		-	-	4	-	-	-0	-	+	?	?
77 K/100% H ₂	-	-	-	-	-	-	-	-	-	+	?	?
Each type of sensor is ev Detection (D) (a) Detects (+) (b) Inoperative (-)	aluated fo	r detect	tion, res	Respo	onse tir Less tl Less tl	power r ne (RT) nan 3 s nan 45 s er that 4	(+) s (0)	ents ac	cording	Pow requ (a		ts (PR) (+)
? Indicates unknown or n	ot availabl	e.		(0)	1		(/				.,	.,
^a Hunter 1992												

Table A6.3 — Sensitivity limits of hydrogen detectors^a

	Minimum detection limits, average values									
Principle		In air		In nitrogen						
Fillicipie	(atm-cc/s)	Hydrogen (%)	LEL (%)	(atm- cc/s)	Hydrogen (%)	Distance [ft (m)]				
Catalytic combustion	8.0	0.02	0.5	80	0.2 ^b	2,000 (609.6) ^c				
Bubble testing	1 x 10 ⁻⁴	NA	NA	1 x 10 ⁻⁴	NA	NA				
Sonic-ultrasonic	1 x 10 ⁻²	NA	NA	1 x 10 ⁻²	NA	100 (30.5) ^d				
Thermal conductivity	1 x 10 ⁻³	5 x 10 ⁻⁴	0.01	1 x 10 ⁻³	5 x 10 ⁻⁴					
Gas density	1 x 10 ⁻²	5 x 10 ⁻³	0.1	1 x 10 ⁻²	5 x 10 ⁻³	NA				
Hydrogen Tape	0.25	1.5	35			(^e)				
Scott-Draeger tubes		0.5	13			NA				
Electrochemical		0.05	1.2		0.05	1,000 (304.8) ^c				
Optical interferometer		0.2	5		0.2	NA				

Dashes indicate information is not available.

- a Rosen, Dayan, and Proffitt 1970
 b Only one commercial catalytic instrument has claimed to detect hydrogen in nitrogen The sensing head is remote from readout
 for pressure differential of 25 psi with orifice of 0.20 in.
 Tape can be placed on suspected leak site and visually checked periodically

Table A6.4 — Typical hydrogen fire detectors^a

Type of detector	Description						
Temperature Sensor	Thermocouple or resistance temperature device (RTD) that detects the heat of the fire.						
Heat Sensitive Cable	Wire or fiber-optic based cable that changes resistance or optical properties if any portion of the cable is exposed to high temperatures or is burned through.						
Optical	Ultraviolet, mid/near-infrared, and thermal infrared detectors for the detection of radiation emitted by the hydrogen flame. Infrared detectors must be optimized for hydrogen flame emissions that are not the same as hydrocarbon fires.						
Broadband Imaging	Thermal or mid-infrared imaging systems effectively image hydrogen flames but require an operator to interpret the image for detection of fire.						
Narrow band Imaging	Band-pass filters centered around the 950, 1100, and 1400 nm peaks can produce adequate images with low-cost silicon CCD cameras, image converter tubes, and vidicon systems. The filters must be carefully selected to block unwanted solar background while optimizing the imaging band for atmospheric transmission of the hydrogen fire radiation.						
Broom/Dust	Putting flammable objects or dust particles into a hydrogen flame will cause the flame to emit in the visible spectrum. Corn straw brooms, dirt, and dry fire extinguishers have been used for this purpose.						
Barnes, H. L. Private cor	^a Barnes, H. L. Private communication, NASA Stennis Space Center (1994)						

A.7 Accidents Involving Hydrogen

Table A7.1 — Hydrogen accidents – industrial^{a, b}

Category	Number of accidents	Percentage total accidents
Undetected Leaks	32	22
Hydrogen-oxygen off-gassing explosions	25	17
Piping and pressure vessel ruptures	21	14
Inadequate inert gas purging	12	8
Vent and exhaust system incidents	10	7
Hydrogen-chlorine incidents	10	7
Others	35	25
Total	145	100
^a Zalosh and Short 1978a ^b Zalosh and Short 1978b		

Table A7.2 — Hydrogen accidents - ammonia plants^a

Classification	Number
Gaskets:	46
Equipment flanges	23
Piping flanges	16
Valve flanges	7
Valve packing	10
Oil leaks	24
Transfer header	9
Auxiliary boiler	8
Primary reformer	7
Cooling tower	3
Electrical	2
Miscellaneous	16
^a Williams 1978	

Table A7.3 — Hydrogen accidents – aerospace^a

Description	Accidents involving release of hydrogen	Percentage of total accidents
Accidents involving release of liquid or	87	81
gaseous hydrogen		
Location of hydrogen release:		
To atmosphere	71 ^b	66
To enclosures (piping, containers, etc.)	26 ^b	24
Ignition of hydrogen releases:		
To atmosphere	44	41
To enclosures	24	22
a Oudin 4074		

Ordin 1974
 Hydrogen was released to both locations in 10 accidents

Annex B Assessment Examples (Informative)

B.1 Example 1: Detonation of GH₂ with Air/Oxygen

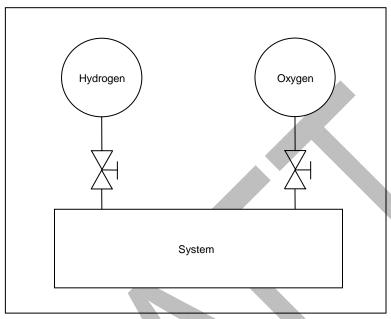


Figure B1.1 — Hydrogen/oxygen system schematic

B.1.1 Statement of Assessment

The inadvertent introduction of GH₂ into a volume containing air-oxygen or the reverse process is the source of many of the industrial and aerospace accidents summarized in Tables A7.1, A7.2 and A7.3. Hazard analysis requires values for pressures and temperatures that occur with detonation of the mixture.

B.1.2 Solution

The Gordon-McBride (1994) program uses Joint Army-Navy-NASA-Air Force (JANNAF) thermodynamic data and performs equilibrium calculations. Table B.1 shows the computed values for a range of mixtures.

The T_1/T_0 and P_1/P_0 ratios give the temperature and pressure rise across the detonation shock. These are equilibrium (Chapman-Jouguet) values. The examples calculated are for a tenfold change in initial pressure (101.3 kPa and 10.1 kPa). The temperature and pressure rise across the detonation shock is similar in relative change.

Table B1.1 — Detonation pressures and temperatures

Volume (% H ₂)	T _o ^a (K)	P。 ^b (kPa)	T ₁ /T _o	P ₁ /P _o		T _o (K)	P _o (kPa)	T₁/T₀	P ₁ /P _o	
	Hydrogen/Air									
18.3	298	101.3	7.657	12.154		298	10.1	7.580	12.111	
25	298	101.3	9.257	14.605		298	10.1	8.870	14.223	
50	298	101.3	8.706	13.713		298	10.1	8.482	13.555	
59	298	101.3	7.678	12.144		298	10.1	7.601	12.119	
			Hydro	ogen/Oxyge	n					
5	298	101.3	3.118	4.880		298	10.1	3.119	4.882	
25	298	101.3	9.034	14.289		298	10.1	8.660	13.896	
50	298	101.3	11.646	17.857		298	10.1	10.537	16.616	
75	298	101.3	12.111	18.671		298	10.1	10.834	17.250	
90	298	101.3	8.576	13.584		298	10.1	8.327	13.393	

^a T = temperature. Subscript "o" indicates initial condition and "1" indicates final condition.

B.2 Example 2: Deflagration of Hydrogen with Air/Oxygen

B.2.1 Statement of Assessment

In those incidents where hydrogen is inadvertently mixed with air or oxygen (see Figure B.1) and only deflagration occurs, the potential hazards are transformation to detonation, fire damage to surrounding equipment or injury to personnel and potential explosion of the fire heating the contents of its vessel. Analysis of the latter case gives the designer an estimate of the pressure that could occur within the vessel.

Only mixtures that fall within the flammability limits shown in Figure A.1 need to be considered. To use Figure A.1, consider points in the lower portion of the figure. A point defined by 10% hydrogen/10% oxygen/80% nitrogen is flammable. A point defined by 2% hydrogen/3% oxygen/95% nitrogen is not flammable.

B.2.2 Solution

The calculation involves a given amount of hydrogen and oxidizer mixed in a specific volume. The system shown in the schematic (Figure B.1) is assumed to be 2 m³. The temperature and pressure in the vessel for a range of compositions is given in Table B.2. The Gordon-McBride (1994) computer code provides the computations.

Table B2.1 — Deflagration pressures

Volume	T _o	Po	T _f ^a	P_f^a		T _o	Po	T_f	P _f	
(% H ₂)	(K)	(kPa)	(K)	(kPa)		(K)	(kPa)	(K)	(kPa)	
Hydrogen/Air										
5	298	101.3	707.9	234.7		273	101.3	684.3	247.6	
25	298	101.3	2,159.2	643.8		273	101.3	2,141.9	697.0	
50	298	101.3	1,937.9	590.0		273	101.3	1,917.7	637.3	
75	298	101.3	1,165.7	375.6		273	101.3	1,142.6	401.9	
Hydrogen/Oxygen										
5	298	101.3	694.2	230.1		273	101.3	671.6	243.0	
25	298	101.3	2,134.5	639.1		273	101.3	2,118.3	692.2	
50	298	101.3	2,913.0	808.5		273	101.3	2,908.3	0.088	
75	298	101.3	3,003.4	837.5		273	101.3	2,999.2	911.6	
90	298	101.3	1,899.2	581.4		273	101.3	1,878.6	612.2	
95	298	101.3	1,132.8	365.9		273	101.3	1,132.8	399.4	

^a T_f and P_f are the final temperature and pressure that would occur in the fixed volume (2 m³) when thermodynamic equilibrium occurred.

b P = pressure

B.3 Example 3: Calculation of the Pressure Rise with Temperature for Both LH₂ and SLH₂

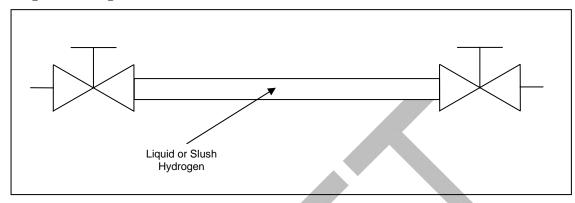


Figure B3.1 — Flow schematic

B.3.1 Statement of Assessment

The possibility of liquid lockup, the blocking of a section of transfer line completely filled (no ullage) with LH₂ or SLH₂, can be safely avoided with proper design. Should such a situation occur, the resulting pressures as the system heats can lead to system damage or hydrogen leakage. Heating occurs through normal operation because there is a significant temperature difference between the LH₂ or SLH₂ and surroundings (at ambient). Standard storage system designs usually assume a heat leak equivalent to 0.5 %/day of the liquid contents.

B.3.2 Solution

The liquid lockup calculation gives the following pressure increase for the corresponding temperature increase. The calculation follows:

$$\left(\frac{\partial P}{\partial T}\right)_{V} = -\frac{\left(\frac{\partial V}{\partial T}\right)_{P}}{\left(\frac{\partial V}{\partial P}\right)_{T}} = \frac{\alpha}{\kappa}$$
(B1)

where:

 α is the coefficient of thermal expansion

κ is the coefficient of isothermal compressibility (Lewis and Randall 1961)

This can be integrated (assuming constant property values) to obtain the following:

$$P = \frac{\alpha}{\kappa} \Delta T + P_0$$
 (B2)

At 20.2 K and $P_0 = 0.101 \text{ MPa}$

$$\alpha = 0.01638 \text{ K}^{-1}$$

$$\kappa = \frac{1}{50.4463} \text{ MPa}^{-1}$$

The property values are from McCarty, Hord, and Roder (1981). Results are given in Table B.3.

Table B3.1 — Liquid-lockup pressure change

Given: LH ₂ at T ₀ = 15 K						
ΔΤ	P					
(K)	[kPa (psia)]					
0.5	413 (60)					
1.0	826 (120)					
5.0	4,130 (600)					
10.0	8,260 (1,200)					

The pressure rise for SLH_2 can occur at constant temperature; the partial molar volume of solid is less than that of liquid: hence, the melting of solid hydrogen increases the volume of liquid. The following values for SLH_2 and LH_2 are obtained from Table A.1:

density
$$LH_2 = 77.03 \text{ kg/m}^3$$

density $SLH_2 (50\% \text{ mass}) = 81.50 \text{ kg/m}^3$

One cubic meter of 50% mass SLH_2 contains $81.50 \, kg$; therefore, 50% mass as LH_2 would occupy $1.06 \, m^3$. Under a liquid lockup situation, the melting of the solid hydrogen would lead to the formation of increased volume. If no ullage were present the system pressure would rise; however, as the pressure rises, the melting temperature changes (Figure A1.10). The actual system pressure would be increasing and if the temperature rose $0.4 \, K$, the melting pressure of the solid would be $1.2 \, MPa$ plus the corresponding increase caused by the change in temperature of the rest of the liquid (see Section B.3.2.1).

Note: Liquid lockup of cryogenic systems is possible if the LH_2 is isolated (not readily hydraulically connected) so pressure increases within the system are not distributed to a relief valve or burst disc.

B.4 Example 4: Analysis of Heat Leak on LH₂ and Ortho-to-Para Conversion and Resulting Effects on SLH₂ Systems

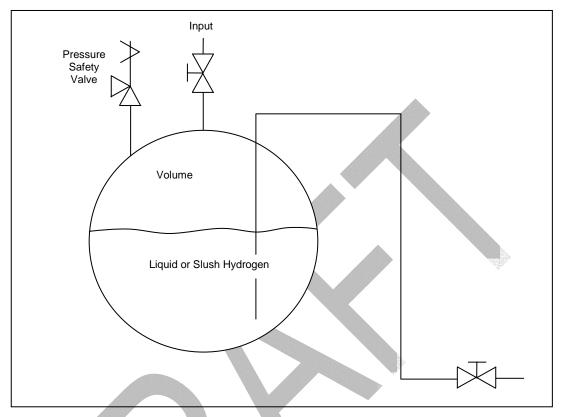


Figure B4.1 — Schematic for pressure buildup example

B.4.1 Statement of Assessment

While LH₂ and SLH₂ storage systems are designed to minimize heat leaks, there is still a finite rate at which thermal energy enters the stored material. The rate of decrease (-dx/dt) of ortho-hydrogen concentration is a bimolecular reaction and can be described by

$$\left(-\frac{dx}{dt}\right) = kx^{2} \tag{B3}$$

where:

x = the fraction of ortho-hydrogen k = the rate constant, 0.0114/h

The spontaneous conversion of ortho-hydrogen to para-hydrogen even occurs in the solid state, in which the conversion rate may be even higher (Edeskuty and Stewart 1996). Assume a rate of 0.5% of the stored contents per 24 h for this example.

B.4.2 Solution

Assume 100 m³ storage (plus 10% ullage) of LH₂ (normal hydrogen). What is the pressure rise per day as a result of evaporated liquid? Neglect effect of pressure increase on evaporation rate. Assume LH₂ normal hydrogen (use Table A1.2).

Data: LH₂ stored at 20.4 K (normal boiling point) P₀ = 101.3 kPa

Amount Evaporated = $0.005 \times 100 \text{ m}^3 = 0.5 \text{ m}^3$

Mass Evaporated = M_{VAP} = 70.91 kg/m³ x 0.5 m³ = 35.5 kg

Density from Table A1.2 includes:

Moles Evaporated = $n_{VAP} = 1.760 \times 10^4$ moles

Initial moles in ullage (assume ideal gas law applies)

$$n_0 = \frac{PV}{RT}$$
 (B4)

$$n_{0} = \frac{101.3 \text{ kPa} \times 10 \text{ m}^{3}}{\left(\frac{101.3 \text{ kPa} \times 0.0224 \text{ m}^{3}}{1 \text{ mol} \times 273 \text{ K}}\right) \times 20.4 \text{ K}} = 6000 \text{ moles}$$

$$P_f = (n_0 + n_v) \left(\frac{RT}{V} \right) \tag{B5}$$

Final pressure:

$$\frac{\left(1.760\times10^{4}+0.6000\times10^{4}\right)\times\left(\frac{101.3\times0.0224}{1\,\text{mol}\times273\,\text{K}}\right)\times\left(20.4\,\text{K}\right)}{10\,\text{m}^{3}}=400\,\text{kPa}\left(58\,\text{psia}\right)$$

If the compressibility of the hydrogen vapor is considered Z = 0.905 (Table A1.2) the final pressure is 362 kPa (52.5 psia).

Assume 100 m³ storage (plus 10% ullage) of SLH₂.

The SLH_2 is 50% mass solid and assume the solid initially is 80% para-hydrogen and 20% orthohydrogen.

Because the equilibrium vapor pressure of SLH₂ is 7.20 kPa (Table A1.2), assume the SLH₂ is under a blanket of helium to bring the initial pressure to 101.3 kPa.

The equilibrium temperature of the SLH_2 is 13.96 K; therefore, the temperature difference for heat leak is greater than in the LH_2 case and 0.5 %/day rate will assume an appropriate amount of solid-liquid phase change.

Total initial mass LH_2 = 4,075 kg Total initial mass solid = 4,075 kg Initial mass para solid = 3,260 kg Initial mass ortho solid = 815 kg

Assume the total thermal energy entering the system by the heat leak is the same as in Section B.4.2.1.

$$Q = M_{vap} x H_{vap}$$

$$Q = 35.5 kg x 10^3 g/kg x 446 J/g = 1.583 x 10^7 J$$
(B6)

Latent heat of vaporization from Table A1.2 = 446 J/g.

Thermal energy from ortho-to-para conversion is:

$$\Delta H_{CONV} = 815 \text{ kg x } 10^3 \text{ g/kg x } 525 \text{ J/g} = 4.279 \text{ x } 10^8 \text{ J}$$

Enthalpy of conversion from Figure A1.2 = 525 J/g.

Total Solid Melted =
$$\frac{(1.583 \times 10^7 + 42.79 \times 10^7)}{58.1}$$
 = 7611 kg (B7)

Latent heat of fusion from Table A1.2 = 58.1 J/g.

The combined heat leak and ortho-to-para conversion would result in sufficient thermal energy to melt all the solid because there was originally 4,075 kg of solid hydrogen. This result points to the need for lower heat input or continuous regeneration of SLH₂. If this is accomplished, the ortho-to-para conversion could be accomplished external to the storage vessel and with external regeneration of solid the vessel pressure could be maintained at its original value. It is also important to note that the equilibrium triple point pressure is 7.20 kPa and without the helium blanket the storage vessel would be at negative pressure with respect to ambient.

B.5 Example 5: Amount of Solid Insulation (Not Vacuum) Required for a Specified Test Line

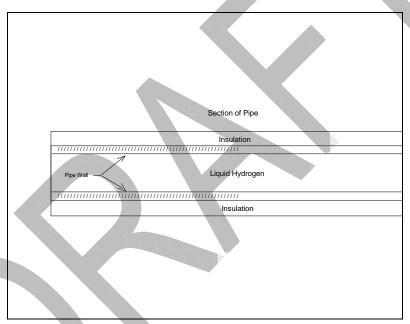


Figure B5.1 — Insulated liquid hydrogen transfer line schematic

B.5.1 Statement of Assessment

Given: 5.1 cm (2 in.) ID (nominal) line 304 stainless steel pipe. Generally, liquid flow velocity is less than 3 m/s (10 ft/s) and assume heat leak is less than ½% of line capacity when in use at steady rate.

Basis: 10 m line; LH₂ (parahydrogen) at 20.3 K. Line is used to transfer 100.0 m³ LH₂.

Pipe Dimensions:

Length and size 10 m, 5.1 cm (2 in.) Schedule 40 Wall thickness 3.91 mm Inside diameter 52.50 mm Outside diameter 60.33 mm 21.64·10⁻⁴ m² Inside cross section

70.78 kg/m³ Density LH₂ from Table A1.1

 $100.0 \text{ m}^3 \text{ x } 70.78 \text{ kg/m}^3 = 7.078 \text{ x } 10^3 \text{ kg}$ Total mass LH₂

 $7.078 \times 10^3 \text{ kg} (1.0 + 0.005) = 7113.4 \text{ kg}$ Total transferred (with heat leak)

B.5.2 Solution

Total thermal energy, Q_T, leaking into the system, assuming leak only causes phase change, is:

$$Q_T = (7113.4 - 7078)kg \cdot 445.6 \text{ kJ/kg} = 1.577 \text{ x } 10^4 \text{ kJ}$$

where latent heat of vaporization for parahydrogen from Table A1.1 = 445.6 kJ/kg.

Length of time to accomplish operation assuming flow is at 3 m/s (10 ft/s) is:

- Volumetric flow = $3 \text{ m/s x } 21.64 \text{ x } 10^{-4} \text{ m}^2 = 6.492 \text{ x } 10^{-3} \text{ m}^3/\text{s}$
- Time = $100.0 \text{ m}^3/6.495 \text{ x } 10^{-3} \text{ m}^3/\text{s} = 1.5396 \text{ x } 10^4 \text{ s} = 4.3 \text{ h}$
- Inner surface area of pipe = $\pi d_i L = \pi \times 0.05250 \text{ m} \times 10.0 \text{ m} = 1.6493 \text{ m}^2$
- Thermal Flux = $1.577 \times 10^4 \text{ kJ/}(1.6493 \text{ m}^2 \times 4.3 \text{ h}) = 0.618 \text{ kJ/m}^2 \cdot \text{s}$

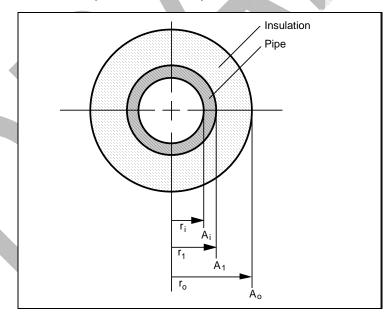


Figure B5.2 — Cross-sectional diagram of insulated LH₂ transfer line

 $q_{SPECIFIED} = 1.6493 \text{ m}^2 \text{ x } 0.618 \text{ kJ/m}^2 \cdot \text{s} = 1019 \text{ W}$

 $q_{CALC} = U_i A_i (T_{AMB} - T_{LH2})$

$$U_{i} = \frac{1}{\frac{1}{h_{i}} + \frac{xA_{i}}{k_{x}A_{lmx}} + \frac{yA_{i}}{k_{v}A_{lmv}} + \frac{A_{i}}{h_{0}A_{0}}}$$
 (Geankoplis 1983) (B8)

 $h_{l} = liquid film transfer coefficient = 2600 \frac{W}{m^{2} \cdot K}$

x = pipe wall thickness = 0.00391 m

$$k_x$$
 = pipe thermal conductivity = $20.0 \frac{W}{m^2 \cdot K}$

A_I = inside pipe surface area = 1.65 m² (Geankoplis 1983)

$$A_{lmx} = \frac{\left(A_{l} - A_{i}\right)}{ln\left(\frac{A_{0}}{A_{i}}\right)} \approx A_{i}$$
 (Geankoplis 1983) (B9)

y = insulation thickness = unknown

 k_y = insulation (Magnesia, 85%) thermal conductivity = 0.05 $\frac{W}{m^2 \cdot K}$

$$A_{lmx} = \frac{A_0 - A_i}{ln\left(\frac{A_0}{A_l}\right)} \approx \frac{A_0 - A_i}{ln\left(\frac{A_0}{A_i}\right)}$$
(B10)

 h_0 = outside film transfer coefficient = $\frac{W}{m^2 \cdot K}$

 A_0 = outside area of insulation

The problem is given q, $T_{amb},\,T_{LH2},$ and all parameter values solve for $r_0\to A_0$

$$U_{i} = \frac{1}{0.000038 + 0.00024 + \frac{33.0y}{A_{lmy}} + \frac{0.33}{A_{o}}}$$
(B11)

B.5.3 Trial-and-Error Solution

Assume a value for r_0 , solve for U_i , solve for q_{CALC} . Does $q_{CALC} = q_{SPECIFIED}$?

Let y = 15 cm (6 in.); therefore, $r_0 = 0.183$ m

$$y = 0.152 \text{ m}$$

 $A_0 = 11.5 \text{ m}^2$
 $A_{lmy} = 5.07 \text{ m}^2$

$$U_i = \frac{1}{0.00038 + 0.00024 + 0.989 + 0.029} = 0.981 \frac{W}{m^2 \cdot K}$$

 $q_{CALC} = 0.981(1.65)(298-20.3) = 449 W$

 $q_{CALC} < q_{SPECIFIED}$; therefore, 15 cm (6 in.) of magnesia insulation would suffice.

Let y = 8 cm (3 in.); therefore, $r_0 = 0.1064 \text{ m}$

$$y = 0.0762 \text{ m}$$

 $A_0 = 6.68 \text{ m}^2$

$$A_{lmy} = 3.6 \text{ m}^2$$

$$U_i = \frac{1}{0.00038 + 0.00024 + 0.698 + 0.0494} = 1337 \frac{W}{m^2 \cdot K}$$

$$q_{CALC} = 1.337(1.65)(298-20.3) = 613 \text{ W}$$

 $q_{CALC} < q_{SPECIFIED}$; therefore, 8 cm (3 in.) of magnesia insulation would suffice.

In comparison an uninsulated line would result in:

$$q_{CALC} = \frac{1}{0.00038 + 0.00024 + 0.2} (1.65)(278) = 2286W$$

twice the q_{SPECIFIED}; therefore, it is not acceptable.

Note: Under the assumed heat leak (0.5 %) 393 m³ of GH_2 is formed. It is realistic to expect that this is unacceptable; therefore, the rate of heat leak would need to be reduced, i.e., a greater level of insulation would be required. Also, this problem assumed steady state operation and does not address the question of system cool down.

B.5.4 Alternative Assessment

The assumed heat leak corresponds to 100 W/m (460 Btu/ft) for the 5 cm (nominal ID) pipe. As described in the note above, this may be excessive and a reduced heat leak would be required. Given the availability of data on heat leak as a function of insulation thickness for various types of insulation, the designer could readily select sufficient insulation. Figure B.6 provides the necessary information (Stewart and Prenger 1991).

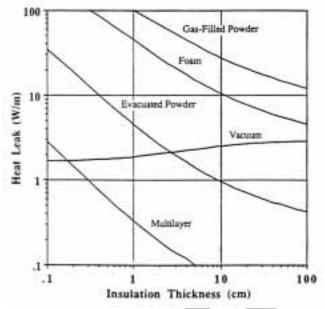


Figure B5.3 — Typical heat leak for various types of thermal insulation (Stewart and Prenger 1991)

B.6 Example 6: Calculation for Siting an LH₂ Storage Dewar

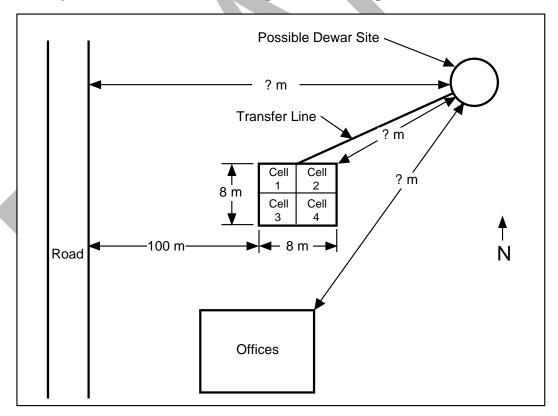


Figure B6.1 — Siting schematic for the LH₂ storage dewar

B.6.1 Statement of Assessment

Assume that given the geographical layout shown in Figure B.7, the problem is to locate a 1000-gal LH₂ dewar to supply experiments conducted in Cell 1 of the schematic.

Assume the following:

Cell construction is reinforced concrete wall with vented, flat-poured concrete roof.

Operation of experimental systems within the cells is controlled remotely from the office structure.

B.6.2 Solution

Total quantity of $LH_2 = 3.785 \text{ m}^3 = 268 \text{ kg } (589 \text{ lb})$

The following separation distances are obtained from the sources indicated.

Table B6.1 — Minimum separation distances for siting the LH₂ dewar in Example 6

	Minimum Separation Distance m (ft)		
	Nonpropellant Use	Propellant Use	
From LH ₂ storage dewar to public roadway	7.6 (25) ^a	183 (600) b,c	
From LH ₂ storage dewar to test cells	1.5 (5) ^a	41 (135) b,d	
From LH ₂ storage dewar offices (place of public assembly)	22.9 (75) ^a	183 (600) b,d	
From Test Cell 1 LH ₂ piping to offices	NS ^e	7.6 (25) ^f	
From Test Cell 1 LH ₂ piping to road	NS	NS	

^a From Table A3.4

B.7 Example 7: Analysis of a Pressure Relief Valve

B.7.1 Statement of Assessment

Each system and item of equipment should be examined for operational safety as set forth by specified requirements. Relief capacity is based on the most severe requirement of a system.

^b From DOD 6055.9 (1992)

^c A dike or barricade could be placed adjacent to the dewar on its west side to reduce the separation distance to the road.

The dewar can be placed on the north side of the cells to reduce hydrogen piping length to Cell 1, assuming cell construction is adequate to provide protection to the office building.

^e NS = Not specified

f From Section 4.6.8

⁻

An early version of this Standard is referenced here and in Annex F, and should be consulted for further information related to this section.

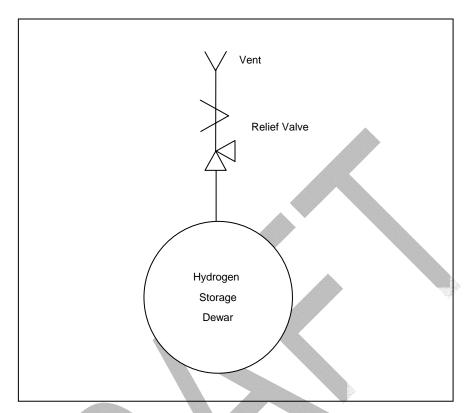


Figure B7.1 — Schematic for relief valve installation

B.7.2 Solution

The sizing of relief devices for safely venting hydrogen vapor or gas requires a calculation of the conditions of critical flow. Critical flow usually will exist for most gases and vapors discharging through the safety valve nozzle and orifice. Critical pressure normally will be found between 53% and 60% of the set pressure; critical flow will exist if the downstream or back pressure on the valve is less than 53% to 60% of the initial relief pressure plus overpressure (Ludwig 1964).

Given: 100 m^3 storage of normal LH₂ (as in Example 4) normal evaporation rate = 35.5 kg/24 h = 1.48 kg/h

Assume insulation failure and an evaporation rate = 0.32 kg/s. The evaporation rate value is calculated based on a spherical volume of 110 m 3 LH $_2$ storage (includes 10% ullage). This surface area for heat transfer would be 111 m 2 and an overall heat transfer coefficient of U = 4.7 W/m 2 ·K (uninsulated system, Example 5) results in heat leak of 1.45 x 10 5 W.

Assume tank relief valve is set at 75 psia and back pressure is 14.7 psia; therefore, critical flow based on criteria given by Ludwig (Ludwig 1964). Also assume that the LH_2 is saturated at the NBP and not at some higher pressure.

The formula for capacity of a relief valve, W, during critical flow with constant backpressure is given by the following equation (ASME BPVC, Ludwig 1964):

$$W = C K A P (M/ZT)^{1/2} lb/h$$
 (B12)

where:

- C = a constant for gas or vapor. C is a function of the specific heat ratio, k ($k = C_p/C_v$). (ASME BPVC, Ludwig 1964)
- K = coefficient of discharge (ASME BPVC), or orifice coefficient (Ludwig 1964)
- A = actual discharge area of the safety relief valve, in² (ASME BPVC), or safety relief valve orifice area, in² (Ludwig 1964)
- P = 1.10 x P_s (P_s is the set pressure), psia (ASME BPVC), or absolute pressure (psia) at inlet including accumulation (Ludwig 1964)
- M = molecular weight of the fluid (ASME BPVC, Ludwig 1964)
- Z = compressibility factor (ASME BPVC, Ludwig 1964)
- T = absolute temperature at the inlet to the relief valve, °R (ASME BPVC, Ludwig 1964)

For this example:

- k = 1.863 for normal hydrogen vapor at NBP from Table A1.2
- C = 377 based on k (ASME BPVC, Ludwig 1964))
- K = 0.97 for nozzle type relief valves (Ludwig 1964)
- $P = 1.10 \times 75 \text{ psia} = 82.5 \text{ psia}$
- M = 2.01594 lb/lb·mol from Table A1.1 (M is same for parahydrogen and normal hydrogen)
- Z = 0.9051 from Table A1.2
- T = 20.390 K from Table A1.2 = 36.7 °R

Given the mass flow of 0.32 kg/s ($2.54 \times 10^3 \text{ lb/h}$) and using equation B11, the area is calculated as 0.3417 in^2 .

The calculated diameter of the safety relief valve orifice is 1.675 cm (0.660 in.).

Note: consideration and allowance should be made because of the variability in the heat leak value. Additional allowance in accordance with the ASME BPVC should be made in the sizing of the relief valve if the tank is exposed to a fire.

B.8 Example 8: Analysis of a Hydrogen Vent/Flare System

B.8.1 Statement of Assessment

Assume venting a steady flow of the same quantity of flow exists as in Example 7 (0.3 kg/s). This flow is the upper limit of the quantity that has been vented without flaring (Section 5.6.2); therefore, a flare should be considered.

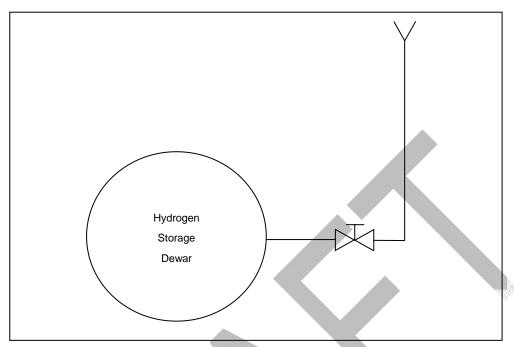


Figure B8.1 — Hydrogen vent/flare system schematic

B.8.2 Solution

Although Example 7 calculated a 2.48-cm (0.975-in.) inside diameter relief nozzle, a 61-cm (24-in.) flare stack is used. Figure A4.1 shows that the hydrogen flow rate (0.32 kg/s) and 61-cm (24-in.) stack diameter results in no flame dip. A 61-cm (24-in.) diameter flare stack would be used to get the high concentrations of air (60 to 85 vol%) without increasing pressure drop and to limit blowout. The flare flame would still show no flame dip if this were the case.

Given: 25% by volume hydrogen concentration (at 0.32 kg H₂/s) the total gas flow would be the following:

$$\frac{n_{_{H2}}}{n_{_{H2}}+n_{_{AIR}}} = 0.25; \qquad n_{_{AIR}} = \frac{0.75}{0.25} \, n_{_{H2}}$$

$$vol\% = mol\%$$
 therefore M_{_{AIR}} = 0.0289 \times n_{_{AIR}} = 12.9 \, kg/s

Velocity at stack exit (61-cm (24-in.) diameter) at:

STP =
$$\frac{(0.45 \text{ kg} \cdot \text{mol/s}) \times (2.2 \text{ lb} \cdot \text{mol/kg} \cdot \text{mol}) \times 359 \text{ ft}^3/\text{lb} \cdot \text{mol}}{3.142 \text{ ft}^2} = 113 \text{ ft/s}$$

According to Figure A4.2, this velocity would result in a stable flame (no blowout); the boundary velocity gradient would be 1356 s⁻¹ using a 2.5-cm (1-in.) boundary layer thickness.

B.9 Example 9: Analysis of the Heat Leak into a LH₂ or SLH₂ Transfer Line and Analysis of the Quantity of LH₂ Consumed to Cool the Transfer Line

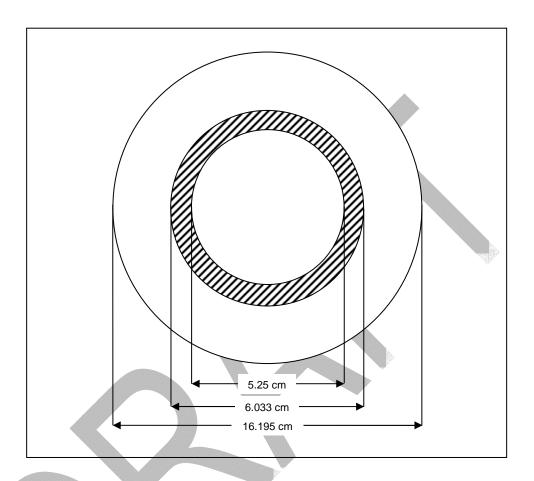


Figure B9.1 — Insulated transfer line configuration

B.9.1 Statement of Assessment

The introduction of LH_2 or SLH_2 into a system presents the problem of cooling the system to the appropriate temperature, 20.3 or 13.8 K. LH_2 will be flashed until the system approaches these temperatures. Too rapid introduction of the cold fluid can cause large stresses in the piping and vessels of the system.

Two calculations are of interest: 1) the total amount of LH₂ or SLH₂ needed to cool the system, and 2) an estimate of the appropriate cooling rate.

B.9.2 Solution

Given: 10 m transfer pipe in Example 5.

Mass steel (304L) pipe =
$$\frac{\pi}{4} \left(\frac{2}{d_o} - \frac{2}{d_i} \right)_{\text{Pipe}} \text{L} \rho_{304SS} = 54.24 \text{ kg}$$

Mass insulation (85% Magnesia) =
$$\frac{\pi}{4} \left(\frac{2}{d_o} - \frac{2}{d_i}\right)_{lnsul} L \rho_{lsul} = 48.06 \text{ kg}$$

The flow rate of Example 5 is

$$\frac{7.1134 \times 10^3 \text{ kg}}{4.3 \text{ hr} \times 3600 \text{ s/h}} \times \left(\frac{2.2 \text{lb}}{\text{kg}}\right) \times \frac{1}{2 \text{ in.}} = 0.505 \frac{\text{lb}}{\text{s·in.}}$$

Assume the system is to be cooled from 298 to 20.3 K.

 $C_{plnsul} = 0.98 \text{ kJ/kg} \cdot \text{K}$

 $C_{p304SS} = 0.461 \text{ kJ/kg} \cdot \text{K}$

 $r_{304SS} = 7817 \text{ kg/m}^3$

 $r_{lnsul} = 271 \text{ kg/m}^3$

 λ_{LH2} = 899 J/mol = 446 kJ/kg

The total enthalpy change of the system is

$$\begin{split} \Delta H &= M_{304SS} C_{p304SS} \int_{T_1}^{T_2} \!\! dT + M_{Insul} C_{pInsul} \int_{T_1}^{T_2} \!\! dT \\ &= \left(\! 54.24 \! \times \! 0.461 \! + 48.06 \! \times \! 0.98 \right) \!\! \left(\! 298 \! - \! 20.3 \right) \! = 2.002 x 10^4 \ kJ \end{split}$$

This calculation would result in the maximum mass of LH₂ converted to GH₂ because it does not utilize any of the sensible heat of the GH₂ formed (Jacobs 1963).

In changing from 298 K to 20.3 K, there is the possibility of a 0.3% contraction in stainless steel. Figure A4.5 gives the maximum flow rate to avoid too rapid cooling of pipe.

For given pipe:
$$\frac{\text{wall thickness}}{\text{pipe diameter}} = \frac{0.392}{5.25} = 0.075$$

Extrapolation gives a maximum W_{max}/D of 0.1 lb/s·in.

In Example 5, at a steady state, the W_{max}/D was 0.505 lb/s·in.; therefore, the startup (such as the cooldown period) would need to be at a much lower flow rate (by at least a factor of 5). In addition, the 44.9 kg of LH₂ changed to GH₂ would have to be handled by the system if LH₂ is used to cool the system. This solution is for nominal pipe thickness. Consideration of the thick wall section of the piping system, such as a flange, would reduce the flow rate because thermal stresses would be greater in the thick wall section.

B.10 Example 10: Purging a Hydrogen System

B.10.1 Statement of Assessment

The purging of hydrogen from systems prior to maintenance or remodeling or the purging of air from hydrogen storage vessels are important operational procedures.

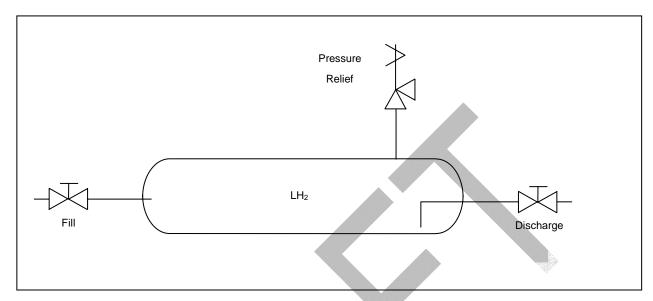


Figure B10.1 — Schematic of a LH₂ storage vessel

Given: 100 m³ LH₂ (plus 10% ullage) storage vessel. Assume LH₂ is para-hydrogen.

B.10.2 Solution

B.10.2.1 Vacuum Purge

Total volume: 110 m³

Assume initial volume filled with air at NTP (293.3 K and 101.3 kPa (68 °F and 14.7 psia)).

Section 7.2.2 stipulates that before filling with LH_2 , the vessel should be evacuated to 1.33 kPa (0.193 psia), repressurized with helium, GN_2 , or GH_2 and vented to atmospheric pressure. Venting must be done safely if GH_2 is used.

What is residual oxygen concentration?

Density air = 1.198 kg/m^3 Initial moles air = $(110 \text{ m}^3 \text{ x} 1.198 \text{ kg/m}^3)/28.82 \text{ kg/kg·mol} = 4.57 \text{ kg·mol}$

Moles air after evacuation (assume ideal gas)

$$n = \frac{pV}{RT} = \frac{1.333 \text{ kPa} \times 110 \text{ m}^3}{\left(\frac{101.3 \text{ kPa} \times 22.4 \text{ m}^3}{1 \text{kg} \cdot \text{mol} \times 273 \text{ K}}\right) \times 293.3 \text{ K}} = 0.0600 \text{ kg mol}$$

Assume vessel repressurized to 25 psig = 273.7 kPa (39.7 psia)

Total moles at pressure:

$$= \frac{273.7 \text{ kPa} \times 110 \text{m}^3}{\left(\frac{101.3 \text{ kPa} \times 22.4 \text{ m}^3}{1 \text{kg mol} \times 273 \text{ K}}\right) \times (293 \text{ K})} = 12.36$$

Therefore; total GN_2 added = 12.36-0.0600 kg·mol = 12.30 kg·mol

Therefore: total O_2 moles = 0.0600 x 0.21 = 0.013 kg·mol

Therefore; percent oxygen concentration = $(0.013/12.36) \times 100 = 0.1\%$

It is important to remember that if LH_2 is to be stored in the vessel, oxygen and nitrogen can condense and solidify. Therefore, the use of helium as a purge gas should be considered, or GH_2 should be used to flush residual GN_2 and GOX from the vessel.

If the system is vented to atmospheric and evacuated again to 1.33 kPa (0.193 psia) after repressurization with inert gas to atmospheric, the residual oxygen is 0.000062 kg·mol or 0.0013%.

B.10.2.2 Alternative Vacuum Purge Method

An alternative purge method is to evacuate and purge with GN₂ for three cycles (omits repressurization with inert gas). Assume purge is at atmospheric pressure.

First cycle: Initial moles = 4.57 kg·mol

Evacuate moles = $0.0600 \text{ kg} \cdot \text{mol}$ Moles oxygen = $0.013 \text{ kg} \cdot \text{mol}$ Pressure to atmospheric adds = $4.51 \text{ kg} \cdot \text{mol} \text{ GN}_2$

Second cycle: Evacuate moles = 0.0600 kg·mol

Moles oxygen = 0.00017 kg·mol kg·mol Pressure to atmospheric adds = 4.51 kg·mol GN₂

Third cycle: Evacuate moles = 0.0600 kg·mol

Moles oxygen = $0.0000022 \text{ kg} \cdot \text{mol}$ Pressure to atmospheric adds = $4.51 \text{ kg} \cdot \text{mol GN}_2$

Final % oxygen concentration = 0.00005%

B.10.2.3 Pressure Purge

The purging of air from new tanks or GH₂ vessels for maintenance can be done using GN₂ or helium until the measured exit concentration is 25% of the LFL (at ambient conditions, less than 1%).

Assume the same storage system initially filled with GH₂ at 101.3 kPa and 293.3 K (68 °F and 14.7 psia).

Density GH_2 (from Table A1.1) = 0.0838 kg/m³

Initial moles $GH_2 = (110 \text{ m}^3 \text{ x } 0.0838 \text{ kg/m}^3)/2.015 \text{ kg/kg·mol} = 4.57 \text{ kg·mol}$

Total moles GN₂ to give 1% = 452 kg·mol

If added to a single charge (assume constant temperature), final vessel pressure would equal:

$$P_f = 101.3 \text{ kPa} (452 + 4.57)/4.57 = 10.1 \text{ MPa} = 1470 \text{ psia}$$

If the vessel cannot contain this pressure, a continuous or semicontinuous batch-type purge must be used.

B.11 Example 11: Dispersion of Hydrogen Release

B.11.1 Statement of Assessment

The accidental leaking or release of hydrogen resulting in flammable mixtures with air presents a safety issue. The hazard analysis should address whether natural dispersion is sufficient to dissipate the mixture to below the LFL or additional operational requirements are needed.

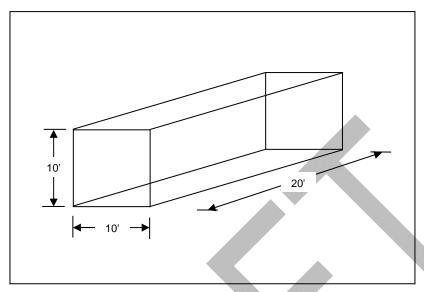


Figure B11.1 — Laboratory space schematic

B.11.2 Solution

B.11.2.1 Instantaneous and Complete Mixing

Minimum standard: 400 CF at 70 °F and 14.7 psia. (Section 1.1.2)

Assume GH₂ released into 56.6 m³ (2,000 ft³) laboratory space.

Given room ventilation at 56.6 m³/min (2,000 ft³/min) (air turnover rate equals once per minute).

Case 1: Assume instantaneous release and mixing; therefore, initial volume concentration in the room = $20\% \, \text{GH}_2$

The concentration of GH₂ is equal to the following:

$$\frac{n}{RT} = \frac{14.7 \text{ psia}}{\left[\frac{(14.7 \text{ psia}) \times (359 \text{ ft}^3)}{1 \text{ lb mol} \times 492 \text{ }^{\circ}R}\right] \times 530 \text{ }^{\circ}R} \times 0.2 = 0.00052 \frac{\text{lb mol}}{\text{ft}^3} = 0.008 \frac{\text{kg mol}}{\text{m}^3}$$

Mass balance of GH₂ in room (in terms of kg·mol)

$$\frac{d}{dt}V_{rm} \times C = -\stackrel{\bullet}{V}C$$
 (B13)

where:

 V_{rm} = volume of room \dot{V} = room ventilation rate C = concentration of H_2 C_o = initial concentration of H_2

$$\ln \frac{C}{C_o} = -\frac{V}{V_{rm}} t$$
(B14)

$$C = C_{o} exp \left(-\frac{\dot{V}}{V_{rm}} \right) t$$
 (B15)

How long does it take to reduce room concentration to less than LFL (4%)?

$$t = \frac{V_{rm}}{V} \ln \frac{C}{C_0} = -\frac{2000 \text{ ft}^3}{2000 \text{ ft}^3/\text{min}} \ln \frac{4}{20}$$

t = 1.6 min

Assume air turnover rate is once every 4 min; therefore, $V = 14.2 \text{ m}^3/\text{min}$ (500 ft³/min) and t = 6.4 min. These values apply only in the case where there is no recirculation of ventilation air.

Case 2: Assuming that leaking GH_2 is instantaneously mixed with room air, what is the maximum leak rate (N_{GH2}) that will always result in concentrations below LFL (4%)?

Mass Balance on GH₂ (in terms of kg · mol):

$$\frac{dV_{m}C}{dt} = \dot{N}_{GH2} - \dot{V}C$$

$$\frac{V_{m}}{\dot{V}}\frac{dC}{dt} + \dot{C} = \frac{\dot{N}_{GH2}}{\dot{V}}$$
(B15)

For V_{rm} / \dot{V} = 1 minute @ turnover rate + 2000 ft³/min, a solution is:

$$C = \frac{\dot{N}_{GH2}}{\dot{V}} \left(1 - e^{-1} \right)$$
 (B16)

at t
$$\rightarrow \infty$$

$$C = \frac{\dot{N}_{GH2}}{\dot{V}}$$
 (B17)

Therefore,
$$N_{GH2} = 1.92 \times 10^{-3} \times 56.63 = 0.109 \text{ kg·mol/min, or } 80 \text{ ft}^3/\text{min of } GH_2$$
 (B18)

$$C < 1.2 \times 10^{-4} \frac{\text{lb mol}}{\text{ft}} \left(\text{or } 1.92 \times 10^{-3} \frac{\text{kg mol}}{\text{m}^3} \right)$$
 (B19)

B.11.2.2 Natural Dissipation

The example above of instantaneous and complete mixing is the first of two limiting assumptions. The second limiting assumption is that the hydrogen released remains as a pure volume and at a time (t = 0), natural dissipation occurs to reduce the concentration of hydrogen.

Assume a spherical cloud of hydrogen 1 m in diameter at ambient conditions (298 K and 101.3 kPa).

Concentration of hydrogen in bubble:

$$\frac{P}{RT} = 0.041 \frac{kg \cdot mol}{m^3} = 0.003 \frac{lb \cdot mol}{ft^3}$$
 (B20)

Assume equal-molal counter diffusion, such as when the hydrogen leaves the bubble it is replaced by air.

Assume the concentration of hydrogen at the surface of the bubble remains approximately zero; the solution can be obtained from analytical solution of diffusion problems (Carslaw and Jaeger 1959).

Concentration at the center of the bubble:

$$C_{C} = 2C_{0} \sum_{n=1}^{\infty} (-1)^{n} e^{-Dn^{2}\pi^{2}t/a^{2}}$$
(B21)

where:

D = hydrogen diffusivity in air = 0.65 cm²/s t = time in seconds a = bubble radius = 50 cm

B.12 Example 12: Certificate Training

Typical material that might be included in certificate training for liquid hydrogen handlers is summarized in this example.

Liquid hydrogen handler's qualification training

Overview

- Basic policy
- Personnel training
- Personnel training must address
- Hydrogen properties
- Ignition sources
- Ignition prevention
- Hydrogen in systems
- Materials to use in hydrogen systems
- Personnel protective equipment
- Cryogenic exposure
- Guidelines for operating procedures
- Transfer precautions
- Loading precautions
- Emergency procedures

Basic policy

Hydrogen can be safely handled like other fuels.

- Safety can be achieved by adherence to the following:
 - Prevent hydrogen leaks
 - Detect accidental leaks and take proper action
 - Prevent hydrogen accumulation
 - Remove likely ignition sources and suspect unknown ignition sources

Personnel training

- Become familiar with hazards of hydrogen
- Recognize human capabilities and limitations
- Become certified for handling LH₂/GH₂
- Understand EMERGENCY Procedures for leaks and spills
- Adhere to accepted standards, guidelines, and codes for designing hydrogen systems

Personnel training must address

- Hazards of hydrogen facilities and operations:
 - Loading and storage systems
 - Purge systems
 - Control sampling and analytical systems
 - Alarm/warning signal systems
 - Ventilation requirements
 - Fire and personnel protection
 - System schematics and emergency procedures

Hydrogen properties

- Cryogenic liquids: Boiling point 20 K (-423 °F)
- Liquid density: 0.07 g/cm³ (water = 1 g/cm³)
- Above 23 K (-418.6 °F), lighter than air
- Flammability limits:
 - Air UFL 74.8%
 - Oxygen UFL 94.0%
 - LFL 4.1%
- Detonation limits in Air: 18.3-59% hydrogen
- Deflagration 5 P_i to 10 P_i, Detonation ≥ 40 P_i
- Flame temperatures (max.): 2,400 K (3,865 °F)
- Hydrogen gas can increase in temperature when expanding

Ignition sources

- Electrical sparks or static electricity (breaking electrical connections, nylon clothing, etc.)
- Friction sparks (metal on metal, stone on stone)
- Impact sparks (sandblasting)
- Autoignition (hot points, etc.) Temperature 584 °C (1084 °F)

Ignition prevention

- Limit sources (remove flammable items and electrical equipment from the area)
- Inert purge boxes around electrical equipment and connections
- Ground equipment
- Provide lightning protection
- Wear nonsparking clothing
- Spark proof tools

Hydrogen in systems

- In LH₂ systems, vents and valves can ice up and fail
- Hydrogen systems should be kept at a positive pressure
- Trapped LH₂ will evaporate, pressurize and rupture lines
 - LH₂ at 14.7 psia, heated to 70 °F, has a pressure of 28,000 psia
- Enclosed or partially enclosed storage areas should be well ventilated

Materials to use in liquid hydrogen systems

- Austenitic SS, Aluminum alloys, copper and alloys
- Nonmetals: Dacron[™] (or the equivalent), Teflon[™] (or the equivalent), PCTFE, Mylar[™] (or the equivalent), and nylon
- Effects and causes of hydrogen embrittlement

Personnel protective equipment

- The best single investment in safety is trained personnel
- Eye, hand, and nonsparking clothing (face shield, gloves, and cotton coveralls)
- Closed toe, nonporous shoes

Cryogenic exposure

Cryogenic burns and injuries

- Remove personnel from danger area
- Ensure you are wearing protective equipment (also breathing air, if necessary)
- Call the EMERGENCY CENTER
- Asphyxiation
 - Often occurs in inert H₂ purge environments

Guidelines for operating procedures

- Provide control of hazards to an acceptable risk
- Prevention, detection, and course of action for hydrogen leaks
- Adequate ventilation guidelines
- Elimination of ignition hazards
- Outline maintenance procedures, if needed

Transfer precautions

- Transfer areas clear of nonessential personnel
- Cancel or discontinue transfers in electrical storms
- Discontinue transfers for leaks or fires
- Isolate, vent, and purge H₂ lines before conducting maintenance
- Remove sources of ignition from transfer areas
- Work in a "buddy system"
- Barricades, warning signs, ropes, etc. establish control

Loading Precautions

- Do not overload a vessel, thermal cycling of relief system
- Oxygen content in a vessel < 2%
- Ground dewar when receiving shipment
- Watch for condensed water on surfaces/leaks
- · No transfers to open mouth dewars/cryopumping
- Cool down storage vessels slowly
- Examine systems for corrosion or blistering

Emergency procedures

- Principle danger from a spill or leak is fire
- For H₂ fires, isolate source and let burn keeping adjacent metal components cool with water

BSR/AIAA G-095-2004

- For a LH₂ spill, rope off area
- For a leak, isolate source, vent, purge, and repair
- If a vessel is burning near other vessels, the burning vessel may be removed if it can be done safely
- Do NOT flare leaks deliberately
- If annulus is exposed to air, do NOT cool with water
- If a LH₂ vessel overturns, try venting through a liquid outlet if this will allow the ullage to vent



Annex C Scaling Laws, Explosions, Blast Effects, and Fragmentation (Informative)

C.1 Scaling Laws

A comprehensive review of accidental explosions has been made by Strehlow and Baker (1975). The review characterizes explosions by type, discusses the various scaling laws, and summarizes nonideal blast wave behavior and the mechanisms by which blast waves produce damage (Stull 1977; DoD 6055.9).

High explosives or nuclear weapons have mainly been used to produce the waves in the classical experimental work on blast waves. The intermediate- and far-field waves generally, quite closely resemble the waves predicted from point-source theory, and to this extent high explosives or nuclear explosions can be considered ideal.

A point-source blast wave is a blast wave conceptually produced by the instantaneous deposition of a fixed quantity of energy at an infinitesimal point in a uniform atmosphere. Essentially there are three regions of interest as a point-source wave propagates away from its source:

- 1) The near-field wave in which pressures are so large external pressure (or counter-pressure) can be neglected.
- 2) An intermediate region of extreme practical importance because the overpressure and impulse are sufficiently high to do significant damage.
- A far-field region that yields to an analytic approximation such that the positive overpressure portion of the curve for large distances can easily be constructed from the overpressure-time curve at one farfield position.

Scaling the properties of point-source blast waves is common practice and subject to cube-root scaling (Sach's law). A given pressure theoretically will occur at a distance from an explosion proportional to the cube root of the energy yield. Full-scale tests have shown this relationship between distance and energy yield to hold over a wide range of explosive weights. According to Sach's law (Bodurtha 1980), if d_1 is the distance from a reference explosion of a mass of W_1 at which a specified hydrostatic overpressure or dynamic pressure is found, for any explosion of a mass of W_2 , these same pressures will occur at a distance, d_2 , given by Equation C1:

$$\frac{d}{d_1} = \left(\frac{W}{W_1}\right)^{1/3} \tag{C1}$$

Plots of overpressures for various explosive weights consequently can be superimposed on the curve for 0.45 kg (1 lb) of explosive if, instead of distance, the distance divided by the cube root of the weight is plotted against overpressure. This correlating parameter (d/W)^{1/3}, called scaled distance, is used to simplify the presentation of the blast wave characteristics.

Cube-root scaling also can be applied to arrival time of the shock front, positive-phase duration, and impulse. The distances concerned also are scaled according to the cube-root law. The relationships can be expressed in the forms:

$$t/t_1 = d/d_1 = (W/W_1)^{1/3}$$

$$I/I_1 = d/d_1 = (W/W_1)^{1/3}$$

where t_1 represents arrival time or positive-phase duration and I_1 is the impulse for the reference explosion W₁; as before, d_1 and d are distances from ground zero. If W_1 is taken as 0.45 kg (1 lb), the various quantities are related as:

 $t = t_1 W^{1/3}$ at a distance $d = d_1 W^{1/3}$ and

 $I = I_1 W^{1/3}$ at a distance $d = d_1 W^{1/3}$.

No general laws exist for scaling blast waves from nonideal explosions because not all the physical parameters affecting such explosions are known. The general concept of equivalence for a nonideal explosion is not well understood. The near-field overpressures usually are much lower than those of a point-source explosion that produces the equivalent far-field overpressure, but it is not obvious exactly what the relationship between near- and far-field behavior should be or how this relationship differs with the type of accidental explosion. It is also not obvious how to evaluate the blast damage of any particular type of accidental explosion or how much the damage depends on the type of explosion.

The comparison between ideal and accidental explosions is inexact because propellant explosions are not considered point sources. The concept of TNT equivalence, widely used in safety studies, is also very inexact and may be quite misleading. Scaling laws for nonideal explosions are not known exactly, but they can be easily developed after the physics of such explosions is well known. The scaling laws likely will be variants on Sach's law (Strehlow and Baker 1975; CPIA 1984).

Theoretical work suggests that distances at which the pressure levels are over approximately 101.3 kPa (14.7 psi) for liquid oxygen (LOX)-liquid hydrogen (LH₂) explosions, the TNT equivalent in terms of peak pressure is about 0.07. The TNT equivalent is about 1 for pressure levels from 101.3 kPa to 0.7 kPa (14.7 psi to 0.1 psi), and about 2.0 below 0.7 kPa (0.1 psi).

These numbers mean that to generate the same pressure-distance relationship as 0.45 kg (1 lb) of TNT at 101.3 kPa (14.7 psi) and above, it takes about 6.5 kg (14.3 lb) of LH₂ and LOX; from 101.3 kPa to 0.7 kPa (14.7 psi to 0.1 psi), about 0.45 kg (1 lb); and at less than 6.9 kPa (0.1 psi) only 0.23 kg (0.5 lb). Correlation with damaging effects on buildings, vehicles, humans, etc., can be made from existing methods and data in the literature if blast wave characteristics can be defined for accidental explosions (CPIA 1984; Baker et al. 1978; Army Material Command Program AMCP-706-180). Fragmentation patterns from accidental explosions and the damaging effects of these fragments are quite difficult to predict.

C.2 Types of Explosions

C.2.1 Explosions in Buildings

Explosions in buildings are of three main types, increasing in severity from Type A to Type C:

- 1) Type A: A spill of some combustible material and a slow deflagration wave or flashback fire causes a relatively slow buildup of pressure in the building.
- 2) Type B: A piece of equipment explodes and produces a blast wave inside the building that damages the structure or is relieved by venting.
- 3) Type C: A leak occurs, but the combustible mixture that forms detonates.

The degree of confinement or the bursting pressure of the vessel or building, for the first and second types of explosion, determines the nature of the blast wave generated and damage patterns. The blast wave behavior and damage patterns in a detonative combustion (third type) primarily are determined by the behavior of the detonation and are only modified by the confinement.

C.2.2 Tank Ruptures

A rupture followed by combustion is a very special type of explosion that primarily occurs when a tank of liquefied fuel, under pressure, is heated by an external fire, following an accident, until the tank vents and torches. The heating of the venting tank needs to be sufficiently intense to cause the internal pressure to rise above the bursting pressure of the tank for an explosion to occur, even with venting. This type of explosion has three distinct damage-producing effects:

- A blast wave caused by internal pressure relief
- A fireball caused by subsequent massive burning of the tank's contents in air
- Large fragments scattered for long distances because of the ductile nature of the rupture of the tank and rocketing of pieces by reaction forces

No single TNT equivalent can be used to describe the blast generated by a rupturing pressure vessel. The tank-rupture blast pressures, combined with the positive shock wave durations, yield positive values of shock wave impulse with an impulse-distance relationship similar in slope to that for TNT. Impulses for tank rupture and the TNT equivalent are not significantly different quantitatively for large, high-pressure vessels.

A general comparison of blast and fragment parameters generated by tank rupture and an equivalent TNT charge shows that side-on pressures, (pressures measured perpendicular to the direction of the shock wave) are higher for TNT above 69 kPa to 41 kPa (10 psi to 6 psi) and lower for TNT at pressures below these values. Face-on tank pressures (pressures measured normal to the incident shock wave) show a similar relationship to face-on TNT pressures. Positive shock wave durations are longer for tank rupture than for TNT. Impulse, face-on and side-on, are similar for TNT and tank rupture. Damage, depending on distance, may be greater for tank rupture. Tank-rupture fragments are larger than would be expected from a cased TNT charge. Fragment velocities are higher for a cased TNT charge than for tank rupture (Baker et al. 1974 and 1978).

C.2.3 Vapor Cloud Explosions

The visual sequence of events in a vapor cloud explosion follows:

- A massive release of a combustible fuel
- A reasonable delay in ignition, 30 s to 30 min
- Ignition of the cloud resulting in an explosion

Vapor cloud ignition can lead to two very different types of behavior. A deflagration, initiated by a weak source, will manifest itself as a fireball with an acoustic report and a low velocity displacement of air. In contrast, a strong ignition source capable of creating a shock wave can directly initiate a detonation in the vapor cloud. The shock waves caused by detonation leave the consumed vapor cloud and push on the surroundings producing a destructive blast wave.

Studies using the usual atmospheric dispersion equations have shown that the maximum fraction of the fuel that would be in the combustible range at any one time from a continuous or massive spill would be about 10% (Strehlow 1973). This agrees quite satisfactorily with available data in which the maximum yield based on TNT equivalent weight is about 10% (Baker et al. 1974; Strehlow, Savage and Vance 1972). Current research into the behavior of vapor cloud explosions is of two major types:

- 1) Assessing the behavior of a deflagrative explosion of the cloud
- 2) Assessing the area of cloud dispersion

The blast waves produced by the explosion of liquid propellants accidentally mixed generally are quite irreproducible and difficult to adequately model. Extensive studies of liquid propellant explosions show that the explosions differ from TNT explosions in a number of ways, so the concept of TNT-equivalence quoted in pounds of TNT is far from exact.

C.2.4 Ground-Handling System Explosions

The hazards from accidental explosions in propellant ground-handling systems are similar in many respects to the hazards from such explosions in flight vehicles. The accidents cause damage by air-blast loading, fragment or appurtenance impact, radiation from fireballs, or fire from the ignition of combustible

materials after an explosion (Strehlow and Baker 1975; DoD 6055.9; CPIA 1984; Army Material Command Program AMCP-706-180; Strehlow, Savage, and Vance 1972).

Flight and ground systems can fail by material fatigue caused by overstressing. Many possible causes of flight vehicle explosions (such as loss of thrust during launch, guidance system failure, or rupture of a bulkhead separating a fuel from an oxidizer) are inapplicable for ground-handling systems.

The nature of the hazards is different because ground-handling systems have fewer weight constraints than flight vehicles. The total energy stored in compressed gases or the total chemical energy stored in fuels and oxidants also can be much greater than for many flight systems.

Many more accidental explosions involving fuels and compressed fluids have occurred in ground-handling systems than in flight vehicles, including:

- simple pressure vessel failure caused by fatigue or flaw growth,
- vessel failure induced by impact during a transportation accident,
- vessel failure by overpressure caused by overheating,
- vessel and pipeline failure caused by overpressure, corrosion or erosion, and
- fuel leakage followed by a vapor cloud explosion.

The Workbook for Estimating Effects of Accidental Explosions in Propellant Ground Handling and Transport Systems (Baker et al. 1978) and Assembly and Analysis of Fragmentation Data for Liquid Propellant Vessels (Baker et al. 1974) provide methods for predicting blast and fragment characteristics and effects for a wide range of possible explosion accidents in ground and flight systems. The material allows for the prediction of:

- explosive energy yield or energy release,
- characteristics of blast pressure waves generated by spherical and nonspherical explosions,
- effects of pressure waves on certain classes of targets,
- characteristics of fragments generated by ground equipment explosions, including massive vessel parts that rocket, and
- effects of fragment impact, including effects of fragment revetments on blast waves.

Various safety factors are included in the prediction methods.

C.3 Characteristics of Fragments

Accidental explosions in ground systems tend to produce very different types of fragments or missiles than similar explosions in flight-weight systems. The most striking difference lies in the number of fragments generated, usually much fewer for ground systems than flight systems.

The Workbook for Estimating Effects of Accidental Explosions in Propellant Ground Handling and Transport Systems (Baker et al. 1978) develops methods of predicting velocities and ranges of fragments from bursting vessels. The fragment range information is based on data from various explosion sources.

The fragment range and mass distributions for the various explosion sources are also included in Baker et al. (1978).

C.4 Effects of Barricades on Blast Waves

Specifically, barricades are constructed near potential explosion sources or in front of structures and facilities located near potential explosion sources. They are intended to be protective devices to arrest fragments or attenuate blast waves. Results of analyses and tests show the following:

- Barricades reduce peak pressures and impulses behind the barricades.
- Single-revetted barricades are more efficient in reducing peak pressures and impulses than mounds.
- Values of peak pressure and impulse are greatly influenced by the height above the ground, location
 of the barricade, and barricade dimensions and configuration.

The effects of near-field, single-revetted barricades on peak overpressures and side-on impulses are given in *Workbook for Estimating Effects of Accidental Explosions in Propellant Ground Handling and Transport Systems* (Baker et al. 1978) and *Engineering Design Handbook, Principles of Explosive Behavior* (Army Material Command Program AMCP-706-180 1972). The references also contain curves indicating blast pressures for predicting lung damage and lethality.

C.5 Estimates of Explosive Yields from Compressed Gas Bursts

C.5.1 Compressed Gas Bursts

The various formulas for total energy release in the rupture of a compressed gas container are reviewed in this section. These formulas include Equation C2:

$$E = \left(\frac{P_1 - P_a}{\gamma_1 - 1}\right) V_1 \tag{C2}$$

where:

E = blast yield (energy)

 P_1 = the initial absolute pressure in the vessel

 P_a = the absolute pressure of the outside atmosphere γ_1 = the ratio of specific heats for the gas in the vessel

 V_1 = the initial volume of the vessel

Referring to Equation C2, an estimate based on isentropic expansion from initial burst pressure to atmospheric pressure can be calculated using Equation C3, and

$$E = \frac{P_1 V_1}{\gamma_1^{-1}} \left[1 - \left(\frac{P_a}{P_1} \right)^{(\gamma_1 - 1)/\gamma_1} \right]$$
 (C3)

as a lower limit, the energy released by constant pressure addition to the explosion source region can be calculated using Equation C4:

$$E = P_a (V_f - V_1)$$
 (C4)

where V_f = the final volume occupied by the gas originally in the vessel.

The three equations are given in descending order of total blast energy estimated. The actual blast yield is considered to lie between Equations C3 and C4. Equation C2 gives slightly higher values than does Equation C3, but both are considered to yield overestimates and are very conservative.

The equations given for blast yields are based on the assumption that all the energy that can drive a blast wave does so depending only on the energy release rate. Some energy for real vessels needs to be

absorbed by the vessel as it fractures, in the fracturing process itself and accelerating the vessel fragments to their maximum velocity.

The Workbook for Estimating Effects of Accidental Explosions in Propellant Ground Handling and Transport Systems (Baker et al. 1978) provides methods for estimating the velocity and kinetic energy of the vessel fragments. Also, the workbook reviews the characteristics of blast waves from liquid propellant explosions and spherical gas vessel bursts and their similarities to the differences from waves from condensed high explosives such as TNT.

All blast parameters are plotted as nondimensional and are shown as functions (f_i) of two nondimensional variables P_1/P_a and \overline{R} , where:

$$\overline{R} = \frac{RP_a^{1/3}}{E^{1/3}}$$
 and f_i is $f_i \left(\frac{P_1}{P_a}, \overline{R} \right)$

Values of the following properties can be calculated from the scaled curves:

$$\overline{t}_{a} = \frac{t_{a} P_{a}^{1/3}}{E^{1/3}}$$

$$\overline{T} = \frac{Ta_{a} P_{a}^{1/3}}{E^{1/3}}$$
(C5)

where:

P_a = ambient pressure (absolute)

a_a = ambient sound velocity

P_s = peak static (side-on) overpressure t_a = arrival time of peak overpressure

T = duration of overpressure

I_s = specific impulse

R = radius of blast wave (standoff distance)

 P_1 = internal absolute pressure of sphere

Typical blast pressure histories for a burst of a frangible gas sphere are given in Baker et al. (1974) and Adamczyk and Strehlow (1977). Characteristics are a pronounced negative phase compared to the first positive phase and the strong second shock wave. By contrast, waves from condensed explosives show much smaller negative phases and seldom have a discernible second shock.

Peak overpressures and shock wave impulse values from a 55 MPa gage (8000 psig) and a 4.1 MPa gage (600 psig) tank rupture are given in Adamczyk and Strehlow (1977) and Strehlow and Ricker (1976). The term "strength," used in these references, refers to several characteristics of a blast wave that relate to the potential of the wave to cause damage and is defined as follows:

- Peak overpressure: The static pressure (often called side-on pressure) is greatest at the wave front.
 This is the peak overpressure, generally reported as pounds/square inch above atmospheric pressure.
- Duration: After the wave front passes, the static pressure falls to slightly below atmospheric. The
 duration of the positive phase the time required to drop the peak overpressure to atmospheric
 pressure is of greatest significance in causing damage.
- Blast-wind velocity: Behind the front of the blast wave the air moves at considerable speed in the same direction as the wave. A peak overpressure of 34.5 kPa (5 psi) will be accompanied by a 72 m/s (236 ft/s) wind for example.
- Dynamic overpressure: The pressure rise produced when the blast wind is brought to rest is called the dynamic overpressure.
- Peak reflected overpressure: The airflow will be stopped and a shock wave will reflect backward
 from the surface if a blast wave strikes a surface (such as a wall) at normal incidence. Behind the
 reflected shock the surface briefly will be subjected to the peak reflected overpressure, sometimes
 called the face-on overpressure. It is considerably larger than the stagnation overpressure, the sum
 of the peak and dynamic overpressures.
- **Positive overpressure impulse:** The area under the positive phase of the overpressure time curve at or near the reflecting surface.

C.6 Degrees of Hazard

Hazards with hydrogen may vary depending on the specific location. The hazards are most severe at range launch pads. The proximity of hydrogen and oxidizers, launchings, nearby facilities, lift-off problems, and possibilities of fallback make these operations most hazardous. When a combination of propellants are used, such as a liquid fuel and a liquid oxidizer, the liquid propellant explosive equivalent recommended by DoD 6055.9 should be used.

Hazards at static test stands, where heavier tankage and greater controls are used, are lower than those at launch pads. Large storage facilities are not normally involved in feeding the engine during tests. Also, facility design should limit any mixing of propellants, reducing the hazard potential.

Cold-flow test operations in which the fuel and oxidizer have completely separate, isolated systems are governed by fire and fragment hazards.

Bulk and temporary storage facilities not directly connected to the launch and test operations are the least hazardous. Pipelines used for transferring propellants should be located in accordance with DoD 6055.9.

C.7 Additional Guidelines

Additional guidelines for estimating explosion damage and designs for limiting explosion damage are presented in *Design for Limiting Explosion Damage* (Lawrence and Johnson 1974), *Guidelines for Estimating Damage Explosion* (Brasie and Simpson 1968), *Structures to Resist the Effects of Accidental Explosions* (Department of the Army TM5-1300), and *Analysis of Hydrogen Explosion Hazards* (Porter 1982).

The thermophysical properties of hydrogen are summarized in *Selected Properties of Hydrogen* (McCarty, Hord, and Roder 1981).

Annex D Codes, Standards and Regulations (Informative)

D.1 General

Annex D gives a brief description and scope of the codes, standards, and regulations applicable for hydrogen systems.

Standards, such as the ASME BPVC and NFPA 50B, are not mandatory by themselves, but mandatory compliance with various standards can be mandated by federal, state, or local governments, or by an organization such as NASA.

Federal regulations applying to hydrogen are embodied primarily in 49 CFR and 29 CFR, DOT and OSHA, respectively. The DOT portions apply to the transportation of hydrogen, and the OSHA portion applies to its safe handling in the work place. The DOT classifies and treats gaseous and liquefied hydrogen as a compressed, flammable gas. Hydrogen is classified as a hazardous material in 29 CFR.

Hydrogen storage is separated into two categories in this AIAA guide: nonpropellant and propellant use.

- The **nonpropellant** category involves the storage of GH₂ and LH₂ in which the main safety consideration is release and possible burning of H₂ in air. (see Section D.4)
- The **propellant** category involves the storage and use of LH₂ in an experimental or test facility or launch complex as a propellant, for which the primary safety consideration is pressure rupture and/or the rapid combustion, or detonation, of a hydrogen-oxidizer mixture. (see Section D.5)

There are no NFPA standards specifically for hydrogen pressure piping (as piping is defined in Section D.3.3); however, the Compressed Gas Association has a general standard for piping systems (CGA G-5.4) that is described in Section D.3.4.

ANSI is the administrator and coordinator of the United States private sector voluntary standardization system. ANSI does not itself develop American National Standards; rather, it facilitates development by establishing consensus among qualified groups. ASME and ANSI documents often have the same designation. The designation for the American Nuclear Society on Power Piping can be listed several ways that include ANSI B31.1, ASME B31.1, and ASME B31.1. ASME B31.1 is the newer, most proper designation for this standard. A standard developed by an organization such as ASME does not receive an ANSI designation until it has been approved as an ANS.

D.2 ASME Boiler and Pressure Vessel Code

The ASME BPVC establishes rules of safety governing the design, fabrication, and inspection of boilers and pressure vessels and nuclear power plant components during construction. The objective of the rules is to assure reasonably certain protection of life and property and provide a margin for deterioration in service. Advancements in design and material and the evidence of experience are constantly being added by Addenda. The BPVC is organized in the following sections:

- I Power Boilers
- II Materials
 - Part A Ferrous Material Specifications
 - Part B Nonferrous Material Specifications
 - Part C Specifications for Welding Rods, Electrodes and Filler Metals
 - Part D Properties
- III Rules for Construction of Nuclear Power Plant Components
- IV Heating Boilers
- V Nondestructive Examination
- VI Recommended Rules for the Care and Operation of Heating Boilers
- VII Recommended Guidelines for the Care of Power Boilers
- VIII Pressure Vessels

Division 1

Division 2, Alternative Rules

- IX Welding and Brazing Qualifications
- X Fiber-Reinforced Plastic Pressure Vessels
- XI Rules for In-service Inspection of Nuclear Power Plant Components

Section VIII, Division 1 of the BPVC is commonly specified for the design, fabrication, and testing of storage vessels, for GH₂ and LH₂. Section IX of the BPVC is commonly specified for welding.

29 CFR1910.103 specifies that GH₂ storage containers shall comply with and be designed, constructed, and tested in accordance with appropriate requirements of ASME BPVC, Section VIII — Unfired Pressure Vessels (1968).

29 CFR 1910.103 specifies that LH₂ storage containers shall comply with and be designed, constructed, and tested in accordance with appropriate requirements of ASME BPVC, Section VIII — Unfired Pressure Vessels (1968) or applicable provisions of API Standard 620, *Recommended Rules for Design and Construction of Large, Welded, Low-Pressure Storage Tanks*, Second Edition (June 1963) and Appendix R (April 1965).

D.3 Codes and Standards for Pressure Piping

D.3.1 General

ASME B31, Code for Pressure Piping, sets engineering requirements deemed necessary for the safe design and construction of pressure piping systems. ASME B31 contains basic reference data and formulas necessary for design of pressure piping. It contains prohibitions in areas, practices, or designs that are known to be unsafe. The Code contains warnings or "flags" when caution is known to be necessary, but it is felt that a direct prohibition would be unwise. The Code consists of the following sections:

A13.1	Scheme for the Identification of Piping Systems
B31G	Manual for Determining the Remaining Strength of Corroded Pipelines: A Supplement to B31,
	Code for Pressure Piping
B31.1	Power Piping
B31.2	Fuel Gas Piping
B31.3	Process Piping (formerly Chemical Plant and Petroleum Refinery Piping)

- B31.3 Process Piping (formerly Chemical Plant and Petroleum Refinery Piping)
- B31.4 Liquid Transportation Systems for Hydrocarbons, Liquid Petroleum Gas, Anhydrous Ammonia, and Alcohols
- B31.5 Refrigeration Piping
- B31.8 Gas Transmission and Distribution Piping Systems
- B31.9 Building Services Piping
- B31.11 Slurry Transportation Piping Systems

Sections A13.1, B31.1, and B31.3 of ASME B31 are the most applicable to hydrogen systems.

The development of a code for cryogenic piping (ASME B31.10) was started, but never completed. Cryogenic piping was eventually incorporated into ASME B31.3 rather than having a separate code specifically for cryogenic piping.

The following specifications are made with regard to the piping associated with a GH₂ storage system:

NFPA 50A — ASME B31.3, Chemical Plant and Petroleum Refinery Piping

29 CFR 1910.103 — ANSI B31.1-1967 with addenda B31.1-1969, Industrial Gas and Air Piping, Pressure Piping Section 2

The following specifications are made with regard to the piping associated with a LH₂ storage vessel:

NFPA 50B - ANSI B31.3, Chemical Plant and Petroleum Refinery Piping, with materials

meeting requirements of Chapter III for piping at an operating temperature

below 244 K (-20 °F)

29 CFR 1910.103 - ANSI B31.1-1967 with addenda B31.1-1969, Industrial Gas and Air Piping,

Pressure Piping Section 2, for GH₂ piping at an operating temperature

above 244 K (-20 °F)

- ANSI B31.3-1966, Petroleum Refinery Piping or ANSI B31.5-1966 with

addenda B31.5a-1968, Refrigeration Piping, for GH₂ piping at an operating

temperature below 244 K (-20 °F), and for LH₂ piping

D.3.2 ASME B31.1, Power Piping

ASME B31.1 prescribes minimum requirements for the design, materials, fabrication, erection, test, and inspection of power and auxiliary service piping systems for electrical generation stations, industrial and institutional plants, central and district heating plants, and district heating systems except as limited by the Code. This code covers boiler external piping as defined in the Code for power boilers and high-temperature, high-pressure water boilers.

Power piping systems covered by this code apply to all piping and their component parts within or forming a part of the above-mentioned plants except as excluded in the Code. They include but are not limited to steam, water, oil, gas, and air services.

This code does not apply to the following: piping specifically covered by other Sections of ASME B31 such as:

- · fuel gas piping;
- · pressure vessels covered by the BPVC;
- building heating and distribution steam piping (low pressure);
- roof and floor drains, plumbing, sewers, and sprinkler and other fire protection systems;
- piping for hydraulic or pneumatic tools and their components;
- piping for marine or other installations under Federal control;
- piping for nuclear installations covered by ASME Boiler and Pressure Vessel Code, Section III; and
- building services piping.

Piping as used in this code includes pipe, flanges, bolting, gaskets, valves, relief devices, fittings, and pressure containing portions of other piping components. It also includes hangers and supports and other equipment necessary to prevent overstressing the pressure containing components.

D.3.3 ASME B31.3, Process Piping (formerly, "Chemical Plant and Petroleum Refinery Piping").

ASME B31.3 prescribes minimum requirements for the design, materials, fabrication, erection, test, and inspection of pressure piping systems for a variety of applications, including cryogenic plants, petroleum refineries, chemical plants, and related processing plants and terminals.

ASME B31.3 does not cover the piping associated with a pressure vessel covered by the ASME BPVC. Piping associated with a pressure vessel is covered by the ASME BPVC, NFPA 50A, NFPA 50B, and 29 CFR 1910.103 for hydrogen. Certain piping within a facility may be subject to other codes and standards, including but not limited to the following:

piping for fuel gas from the point of delivery to the connection of each fuel utilization device

- fire protection systems using water, carbon dioxide, Halon, foam, dry and wet chemicals
- medical and laboratory gas systems
- potable hot and cold water; and sewer and drain systems

Piping, as used in ASME B31.3, includes pipe, tubing, flanges, bolting, gaskets, valves, relief devices, fittings, and the pressure containing portions of other piping components. It also includes hangers and supports and other equipment necessary to prevent overstressing pressure containing components.

Piping is considered in ASME B31.3 as the piping that begins when a pressure vessel proper terminates at the following:

- The first circumferential joint for welding end connections
- The face of the first flange in bolted flanged connections
- The first threaded joint in that type of connection and that extends up to and includes the valve or valves on the pressure vessel as required by the ASME BPVC

ASME B31.3 generally does not specify materials to be used in piping systems, but provides guidance and limitations on the selection of some materials acceptable for use in piping systems. The Code provides some useful properties for these materials, such as minimum temperature, and maximum allowable stress values as a function of operating temperature (see summary in Table A5.3).

D.3.4 CGA G5.4, Standard for Hydrogen Piping Systems at Consumer Locations

A standard specifically for hydrogen piping systems is the *Compressed Gas Association's Standard for Hydrogen Piping Systems at Consumer Locations*, CGA G-5.4. This CGA standard describes the specifications and general principles recommended for piping systems for gaseous or liquid hydrogen on premises beginning at the point at which hydrogen enters the distribution piping (the battery limits of the hydrogen storage system) at service pressure to the use point of the hydrogen. The information in CGA G-5.4 is general in nature and intended for use by designers, fabricators, installers, users, and maintainers of hydrogen piping systems and should be of interest to safety personnel, fire departments, building inspectors, and other emergency personnel. CGA G-5.4 specifies piping systems should be designed in accordance with ASME B31.3, *Chemical Plant and Petroleum Refinery Piping*.

D.4 Standards and Regulations for the Commercial, Industrial, and Non-Propellant Use of Hydrogen

D.4.1 NFPA 50A and NFPA 50B

D.4.1.1 General

NFPA 50A and NFPA 50B have a narrow scope of application. They cover bulk storage vessels from the point of fill connection to the point at which hydrogen enters the distribution piping. They do not cover the delivery vehicle or the distribution piping. The QD requirements are key features of the two standards.

The QD requirements of NFPA 50A and 50B are based on the concept that the effects of fire, explosion, and detonation can be reduced to tolerable levels if the source of the hazard is kept far enough from people and other facilities. Having a separation distance between a hydrogen system and people and other equipment reduces confinement, which provides a greater probability that hydrogen from leaks or spills will diffuse and dissipate without contacting an ignition source. A separation distance also provides flame-propagation control; thermal radiation from a fire does not create a situation in which fire from one source is propagated to another combustible material.

NFPA 50B was developed from tested and proven industrial handling and storage techniques for the practical needs of a commercial operation. (One of the activities of the NFPA is the development of codes

and standards to enhance fire safety.) Guidelines of the DoD such as DoD 6055.9 primarily established for explosives and propellants for missile and rocket applications, were considered in the formulation of the NFPA standards for industrial applications. The QD guidelines of the DoD were considered unrealistically severe and did not apply to conventional industrial users. The NFPA standards were developed on a concept based on the maximum credible accidental leakage or spill that could be expected in a given installation. Spills of 18.9 L to 189 L (5 gal to 50 gal) could be expected and would be within the parameters of the standard in servicing a typical 26,500 L (7000 gal) LH₂ customer station using loading and handling techniques developed by commercial companies for example. It was felt that this "reasonable scope of expectation," based on experience, should be recognized as the safety parameter rather than a major catastrophe, such as a falling airplane. The safety philosophy of the standards, initially developed as a CGA standard then later as NFPA standards, may be simply expressed as follows: protect the system from the user, not just the user from the system. The NFPA standard specifications for construction, installation, distance locations, and materials were established to limit hazards so that severe damage to surrounding buildings and personnel would be highly unlikely (Connolly 1967).

NFPA 50A and NFPA 50B do not specify whether the QD guidelines are determined by the hydrogen system exposing the adjacent occupancy, the adjacent occupancy exposing the hydrogen installation, or a mutual exposure. A difference in the hazards between the "business" end of a storage vessel and the "nonbusiness" end of a storage vessel is possible. The business end contains the vessel connections, vaporizers, and other equipment. NFPA 50B addresses the difference by setting different distances for "insulated" versus "noninsulated" portions of the storage vessel; however, the distances in NFPA 50A do not currently reflect any difference in the hazard between the two ends.

The QD guidelines of NFPA 50B are predicated on the installation of an emergency vent system sized to prevent a storage vessel rupture even when the vessel is surrounded by fire.

D.4.1.2 NFPA 50A, Gaseous Hydrogen Systems at Consumer Sites

NFPA 50A covers the requirements for the installation of GH_2 systems on consumer premises that meet the following criteria:

- The hydrogen supply to the consumer premises originates outside the consumer premises
- The hydrogen supply is delivered by mobile equipment

This standard does not apply to single systems using containers having a total hydrogen content of less than 11 m³ (400 ft³). However, this standard applies to individual systems, each having a total hydrogen content of less than 11 m³ (400 ft³) located less than 1.5 m (5 ft) from each other.

This standard does not apply to hydrogen manufacturing plants or other establishments operated by a hydrogen supplier or the supplier's agent for the purpose of storing hydrogen and refilling portable containers, trailers, mobile supply trucks, or tank cars.

The scope, or extent, of the applicability of NFPA 50A is shown in its definition of a GH₂ system. A GH₂ system is defined as "one in which the hydrogen is delivered, stored, and discharged in the gaseous form to consumer's piping. The system includes stationary or movable containers, pressure regulators, pressure relief devices, manifolds, interconnecting piping, and controls. The system terminates at the point at which hydrogen at service pressure first enters the consumer's distribution piping."

D.4.1.3 NFPA 50B, Liquefied Hydrogen Systems at Consumer Sites

NFPA 50B covers the requirements for the installation of LH₂ systems on consumer premises for which the hydrogen supply to the consumer premises originates outside the consumer premises, and is delivered by mobile equipment.

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[†] Bender, F. X. Presentation notes on discussion of NFPA 50A and NFPA 50B.

This standard does not apply to the following:

- Portable containers having a total LH₂ content of less than 150 L (39.7 gal)
- LH₂ manufacturing plants or other establishments operated by a hydrogen supplier or the supplier's agent for the sole purpose of storing LH₂ and refilling portable containers, trailers, mobile supply trucks, or tank cars

The scope, or extent, of the applicability of NFPA 50B is shown in its definition of a LH_2 system. A LH_2 system is defined as "a system into which liquefied hydrogen is delivered and stored and from which it is discharged in the liquid or gaseous form to consumer piping. The system includes stationary or portable containers, including unconnected reserves, pressure regulators, pressure relief devices, manifolds, interconnecting piping, and controls as required. The system originates at the storage container fill connection and terminates at the point hydrogen at service pressure first enters the supply line."

D.4.2 Code of Federal Regulations

The CFR is a codification of the general and permanent rules of the Federal Government. The Code is divided into titles, which represent broad areas subject to Federal regulation. The Code titles are divided into chapters, parts, and sections (titles, chapters, and parts may be divided into subtitles, subchapters, and subparts). The titles that are of primary interest to the use of hydrogen include Title 29 — Labor and Title 49 — Transportation. The parts and sections of Title 29 — Labor and Title 49 — Transportation that are of interest for the use of hydrogen are given in Sections D.4.2.1 and D.6, respectively.

D.4.2.1 Title 29 — Labor

Part 1910—Occupational and Health Standards. Part 1910 provides regulations related to safety in the work place. This part of Title 29 is one that is of primary interest to the use of hydrogen. Some sections of Part 1910 that may be applicable for the use of hydrogen include the following:

Subpart E — Means of Egress

1910.38 Employee emergency plans and fire prevention plans

Subpart H — Hazardous Materials (this subpart addresses the safe handling of hazardous materials in the workplace)

1910.101	Compressed gases (general requirements)
1910.103	Hydrogen (see Section D.4.2.2 for details of this section)
1910.106	Flammable and combustible liquids
1910.119	Process safety management of highly hazardous chemicals
1910.120	Hazardous waste operations and emergency response

Subpart I — Personal Protective Equipment

1910.132	General requirements
1910.133	Eye and face protection
1910.134	Respiratory protection

Subpart J — General Environmental Controls

1910.146 Permit-required confined spaces

Subpart L — Fire Protection

1910.156 Fire brigades

1910.163 Fixed extinguishing systems, water spray and foam

1910.165 Employee alarm systems

Subpart S — Electrical

1910.307 Hazardous (classified) locations

1910.399 Definitions applicable to this subpart

Subpart Z — Toxic and Hazardous Substances

1910.1027 Cadmium

1910.1200 Hazard communication

Part 1926 — Safety and Health Regulations for Construction. This part is applicable for the construction and construction practices involved in a hydrogen system or facility.

Subpart D — Occupational Health and Environmental Controls

1926.55 Gases, vapors, fumes, dusts, and mists

D.4.2.2 29 CFR 1910.103, Hydrogen

Over time several standards related to hydrogen were developed, especially to give QD recommendations; eventually some of these were incorporated into the CFR, and thus compliance made mandatory. NFPA 50A and 50B for GH_2 and LH_2 storage were incorporated almost completely into 29 CFR 1910.103 for example.

29 CFR 1910.103 applies to the installation GH₂ and LH₂ systems on consumer premises where the hydrogen supply to the consumer premises originates outside the consumer premises and is delivered by mobile equipment.

A gaseous hydrogen system is defined in 29 CFR 1910.103 as an assembly of components to which hydrogen is delivered, stored, and used in the gaseous form. The system may include storage vessels (stationary or mobile), interconnecting piping, manifolds, valves, pressure relief devices, pressure regulators, pumps, vacuum system, expansion joints, gages, and controls. A GH₂ system, as defined in 29 CFR 1910.103, is limited to the bulk storage vessel (and ancillary components) from the point of the fill connection to the point where GH₂ enters the consumer's distribution piping.

A liquid hydrogen system is defined in NFPA 50B as an assembly of components to which hydrogen is delivered, stored, and used in the liquid and/or gaseous form. The system may include storage vessels, piping, valves, relief devices, pumps, vacuum system, expansion joints, gages, and controls. A LH₂ system, as defined in NFPA 50B, is limited to the bulk storage vessel (and ancillary components) from the point of the fill connection to the point where LH₂ and/or GH₂ enters the consumer's distribution piping.

D.5 Standard for the Propellant Use of Liquefied Hydrogen

D.5.1 General

A standard that applies to LH₂ installations where liquid propellants are present and covers all types of liquid propellant storage areas, including missiles, rockets, and multi-compartment tanks in which liquid fuels and liquid oxidizers are stored is DoD 6055.9, Ammunition and Explosives Safety Standards. This explosive safety standard is designed to manage risks associated with DoD-titled ammunition and explosives by providing protection criteria to minimize serious injury, loss of life, and damage to property.

The purpose of DoD 6055.9 is to establish uniform safety standards applicable to:

- Ammunition and explosives (including liquid propellants such as liquid hydrogen,
- Associated personnel and property, and
- Unrelated personnel and property exposed to the potentially damaging effects of an accident involving ammunition and explosives during their development, manufacturing, testing, transportation, handling, storage, maintenance, demilitarization, and disposal.

The intent of DoD 6055.9 is to provide the maximum possible protection to personnel and property, both inside and outside an installation, from the damaging effects of potential accidents involving DoD ammunition and explosives, and to limit the exposure of a minimum number of persons, for a minimum time, to the minimum amount of ammunition and explosives consistent with safe and efficient operations.

The requirements in this standard are considered minimum and greater protection shall be afforded when practical. They apply whenever any explosives, propellants, or similar energetic materials are present on DoD-owned, or –leased, facilities and to U.S.-titled ammunition in host nation facilities.

DoD 6055.9 addresses the following subject areas:

- · Effects of explosives
- Hazard classification, storage principles, and compatibility groups
- Personnel protection and permissible exposure levels
- Construction criteria permitting reduced separation distances
- Electrical standards
- Lightning protection
- Hazard identification for fire fighting and emergency planning
- QD and siting
- Contingencies, combat operations, military operations other than war, and associated training
- Toxic chemical munitions and agents
- Real property contaminated with ammunition, explosives or chemical agents
- Accident notification and reporting requirements
- · Special storage procedures for waste military munitions

D.5.2 Hazards Addressed

The hazards of an explosion addressed by this standard are:

- Blast pressure
- Primary and secondary fragments
- Thermal hazards
- Ground shock and cratering
- Chemical agent hazards

D.5.3 Protection for Personnel and Property

DoD 6055.9 provides blast, fragment, and thermal hazards protection principles that apply to all operations and operational facilities where personnel are exposed to ammunition and explosives hazards during industrial, processing, manufacturing, maintenance, renovation, demilitarization, and similar operations.

DoD 6055.9 requires that personnel be protected from potential blast overpressures, hazardous fragments, and thermal effects when specified hazard assessments indicate the probability of an accidental explosion with attendant overpressures and hazardous fragments, or an accidental flash fire with attendant thermal hazards is above the acceptable risk level as determined on a case-by-case basis.

The protection provided all personnel is required to limit:

- Incident blast overpressure to 15.9 kPa (2.3 psi)
- Fragments to energies of less than 79 J (58 ft-lb)
- Thermal fluxes to 12.56 kW/m² (0.3 calories/(cm²·s))

These protection levels are to be certified through analysis for cases where personnel are at distances less than distances determined by means of a formula of the type $D = K \cdot W^{1/3}$ where D is the distance in feet, W is the net explosive weight in pounds and K = 24 ft/lb^{1/3} (K is a factor depending upon the risk assumed or permitted).

DoD 6055.9 specifies that at operations where intentional ignition/initiation of explosives are conducted, such as function, proof, lot acceptance, testing, and such like, and where shielding is required as determined on a case-by-case basis, protection afforded all personnel must meet the requirements stated above, and must also be capable of:

- Limiting overpressure levels in personnel-occupied areas to satisfy applicable standards
- Containing or defeating all fragments, and
- Limiting thermal flux to Q = 0.62t^{-0.7423} where Q is the thermal flux (calories/cm²·s) and t is the time (in seconds) that a person is exposed to the radiant heat.

Approved shields may be used to provide acceptable protection.

Protective measures that are specified by DoD 6055.9 include:

- Elimination, or positive control, of ignition and initiation stimuli,
- Sufficient distance or barricades to protect from blast or fragments,
- A fire detection and extinguishing system,
- Thermal shielding,
- Personnel protective clothing and equipment, and
- Specified building construction practices.

D.5.4 Construction Criteria

DoD 6055.9 provides safety requirements for construction features and location considerations for a potentially explosive site, and for a site exposed to a potentially explosive site. These siting and construction standards are to be used within the DoD. These requirements are intended to permit reducing separation distances by significantly altering the effects of potential explosions by siting and construction features that:

Limit the amount of explosives involved,

- Attenuate resultant blast overpressure or thermal radiation,
- · Reduce the quantity and range of hazardous fragments and debris,
- Provide protection against explosion communication between adjacent bays or buildings, and
- Ensure against unacceptable damage and injuries in the event of an incident.

D.5.5 QD and Siting

D.5.5.1 General

DoD 6055.9 provides requirements for siting for explosive safety distance criteria. Other separation distances based on criteria for other hazards (such as toxicity, noise, thermal radiation, flight trajectory, fragmentation, and incendiary) may apply, and the greater separation distance shall be used to determine siting and construction of a potentially explosive facility.

The damage or injury potential of explosions is normally determined by:

- The separation distance between a potential explosive site and an exposed site,
- The capability of the potential explosive site to suppress blast overpressure, primary and secondary fragments, and debris, and
- The ability of the exposed site to resist explosion effects.

DoD 6055.9 provides minimum standards that consider the following for separating a potential explosive site from an exposed site:

- Explosion effects
- Suppression
- Resistance

DoD 6055.9 establishes QD relationships for both related, and unrelated, potential exposure sites, with both explosives and nonexplosives exposure sites.

The QD standards provided in DoD 6055.9 are based on permissible exposures for both accidental and intentional detonations.

DoD 6055.9 establishes explosive safety siting criteria (QD relationships) for PESs and an exposure site based on:

- Blast
- Fragment
- Firebrand
- Thermal
- · Ground-shock effects

QD is determined by the effect requiring the greatest separation distance.

D.5.5.2 QD Requirements for Energetic Liquids

QD requirements for the use of LH_2 as a propellant are addressed in the section of DoD 6055.9 that specifies QD requirements for the propellant use of energetic liquids. This section applies to the storage of specified energetic liquids in all types of containers, including rocket and missile tankage. Laboratory quantities of energetic liquids shall be stored and handled as prescribed by the AHJ.

The QD requirements in this section are only based on the energetic liquids' energetic reaction (blast overpressure and container fragmentation). Other QD requirements, such as those for toxicity or potential down-wind location, shall also be considered when selecting a location for storage of energetic liquids. When additional hazards associated with ammunition and explosives are involved, the safety distances prescribed in other sections of DoD6055.9 shall be applied as required. Thus, the QD requirements for an energetic liquid must be based on a determination of the predominant hazard presented by the material in the storage environment.

This section does not govern the storage or handling of energetic liquids for uses other than in space launch vehicles, rockets, missiles, associated static test apparatus, and ammunition and explosives. The standards given in this section are based on the estimated credible damage resulting from an incident without considering probabilities or frequency of occurrence.

The energetic liquids covered by DoD 6055.9 are classified according to compatibility groups. Energetic liquids in the same compatibility group can be stored together, but mixed storage of energetic liquids of different compatibility groups is prohibited with one exception that is permitted for an operationally necessary situation.

The QD standards in DoD 6055.9 for energetic liquids were developed on the basis that the AHJ will ensure that the:

- Materials of construction are compatible with the energetic liquids,
- Facilities are of appropriate design,
- Fire protection and drainage control techniques are employed, and
- Other special controls (for example, nitrogen padding, blanketing, and tank cooling) are used when required.

The total quantity of liquids in a tank, drum, cylinder, or other containers shall be the net weight of the energetic liquids contained therein. The net weight must include the quantity of energetic liquids within any associated piping to the points where positive means are provided for interrupting the flow through the pipe, or interrupting a reaction in the pipe in the event of an incident.

Separation distances shall be measured from the closest hazard source (containers, buildings, segment, or positive cutoff point in piping, whichever is controlling).

The predominant hazard of an individual energetic liquid can vary depending on the location of the energetic liquid storage site and the operations involved. The storage and operations conditions, in order of decreasing hazards, are given in DoD 6055.9 as follows:

- Launch pad
- Static test stand
- Ready storage
- Cold-flow test operation
- Bulk storage
- Rest storage
- Run tankage (operating tankage)
- Pipeline

The **launch pad** is considered the most hazardous because of the:

- Proximity of fuel and oxidizer to each other,
- · Frequency of launchings,
- Lack of restraint of the vehicle after liftoff, and
- Possibility of fallback with resultant dynamic mixing on impact.

The **static test stand** is considered less hazardous than a launch pad because the test items are restrained and subject to better control than launch vehicles. As with the launch pad, the proximity of fuel and oxidizer presents a significant hazard. To reduce this hazard, tankage should be separated and remotely located from the static test stand. The type of construction and protection provided for run tanks can further reduce the hazards associated with a static test stand.

Ready storage is storage that is relatively close to the launch and static test stands; and, normally it is not directly involved in feeding the engine as in the case of run tankage, which is an integral part of all launch and test stand operations. Ready storage is considered less hazardous than static test stands if the facility design prevents fuel and oxidizer mixing and prevents detonation propagation to, or initiation at, the ready storage facility when a mishap occurs at the test stand, on the ground at the launch pad, or at the ready storage area.

Cold-flow test operations are considered less hazardous than ready storage if:

- The design is such that the system is closed except for approved venting,
- The system is completely airtight,
- Fuel and oxidizer never are employed concurrently,
- Each energetic liquid has a completely separate isolated system and fitting types to preclude intermixing, and
- The energetic liquids are of required purity.

Bulk storage is the most remote storage with respect to launch and test operations. It consists of the area, tanks, and other containers therein, used to hold energetic liquids for supplying ready storage and, indirectly, run tankage where no ready storage is available.

Rest storage is temporary-type storage and most closely resembles bulk storage. It is a temporary parking location for barges, trailers, tank cars, and portable hold tanks used for topping operations when these units actually are not engaged in the operation; and for such vehicles when they are unable to empty their cargo promptly into the intended storage container. The transporter is considered a part of that storage to which it is connected during energetic liquids transfer.

Run tankage (operating tankage) consists of the tank and other containers and associated piping used to hold the energetic liquids for directly feeding into the engine or device during operation. The contents of properly separated "run tanks" (operating tankage) and piping are normally considered on the basis of the pertinent hazards for the materials involved, except for quantities of incompatible materials that are or can be in a position to become mixed.

Pipelines used for transport of energetic liquids are considered the least hazardous. A minimum distance (clear zone) of 7.6 m (25 ft) is specified between a pipeline containing an energetic liquid and an inhabited building. An exception to this minimum distance is made for flammable or combustible liquids (such as RP-1, JP-10, and Otto Fuel II) that exhibit normal fire hazards.

DoD 6055.9 specifies QD requirements based on factors such as the following:

The type of facility that is a PES that is involved (static test stand, for example)

- The design of the facility that is a PES (degree of protection provided to limit blast and fragments, for example)
- The operations conducted at the facility that is a PES (for example, engine firing)
- The ability of the exposed site (an inhabited building, for example) to resist possible explosion effects
- The energetic liquids involved (for example, liquid hydrogen and liquid oxygen)
- The possibility of intermixing of the energetic liquids involved
- The compatibility of the energetic liquids involved
- The quantity of each of the energetic liquids involved

DoD 6055.9 specifies that the QD shall be determined on the basis of the explosive equivalent of the mixture for conditions that involve the potential intermixing of incompatible energetic liquids (such as a fuel and an oxidizer) and a resulting explosion with blast overpressure and fragments. For conditions that involve only one energetic liquid (such as bulk storage of a fuel) and the primary hazards that govern are fire and fragments, DoD 6055.9 specifies that the QD shall be determined on the basis of the weight of the energetic liquid, and provides tables of minimum distances to various exposed sites as a function of the weight of the energetic liquid. An example of determining a QD in accordance with DoD 6055.9 is given in Section B.6 of Annex B.

A summary of the hazardous conditions involved, and the QD determination method specified, is given in Table D.1 for each of the hazard locations listed above.

D.6 Regulations for Transportation Equipment and the Transport of Hydrogen

D.6.1 Regulations

Regulations related to transportation equipment and to the transport of hydrogen, are given in 49 CFR, Subtitle B, Chapter I, Subchapters A, B, and C in the various parts of these subchapters as shown in the following outline.

49 CFR - Transportation

Subtitle B - Other Regulations Relating to Transportation

CHAPTER I - RESEARCH AND SPECIAL PROGRAMS ADMINISTRATION.

DEPARTMENT OF TRANSPORTATION

SUBCHAPTER A - HAZARDOUS TRANSPORTATION, OIL

TRANSPORTATION AND PIPELINE SAFETY

Part 100 - [Reserved]

Part 106 - Rule making procedures

Part 107 - Hazardous materials program procedures

Part 110 - Hazardous materials public sector training and planning grants

SUBCHAPTER B - OIL TRANSPORTATION

Part 130 - Oil spill prevention and response plans

SUBCHAPTER C - HAZARDOUS MATERIALS REGULATIONS

Part 171 - General information, regulations, and definitions

Part 172 - Hazardous materials tables and hazardous materials communications regulations

Part 173 - Shippers-general requirements for shipments and packagings

Part 174 - Carriage by rail

Part 175 - Carriage by aircraft

Part 176 - Carriage by vessel

Part 177 - Carriage by public highway

Part 178 - Specifications for packagings

Part 179 - Specifications for tank cars

Part 180 - Continuing qualifications and maintenance of packagings

SUBCHAPTER D - PIPELINE SAFETY

Part 190 - Pipeline safety program procedures

Part 191 - Transportation of natural and other gas by pipeline; annual reports, incident reports, and safety-related conditions

Part 192 - Transportation of natural and other gas by pipeline: minimum Federal safety standards

Part 193 - Liquefied natural gas facilities: Federal safety standards

Part 195 - Transportation of hazardous liquids by pipelines

Part 196 - [Reserved]

Part 197 - [Reserved]

Part 198 - Regulation for grants to aid state pipeline safety programs

Part 199 - Drug testing

D.6.2 Scope of Subchapter C

Subchapter C prescribes the requirements of the DOT governing the transportation of hazardous materials by, and their offering, to the following:

- Carriers by rail car, aircraft, and vessel (water craft such as ship, ferry, and barge)
- Interstate and foreign carriers by motor vehicle
- Intrastate carriers by motor vehicle so far as Subchapter C relates to:
 - hazardous waste
 - hazardous substances
 - flammable cryogenic liquids in portable tanks and cargo tanks
 - marine pollutants

The manufacture, fabrication, marking, maintenance, reconditioning, repairing, or testing of a packaging or container represented, marked, certified, or sold for use in such transportation as described above.

Any person who, under contract with any department, agency, or instrumentality of the executive, legislative, or judicial branch of the Federal Government, transports, or causes to be transported or shipped, a hazardous material or manufacturers, fabricates, marks, maintains, reconditions, repairs, or tests a package or container represented, marked, certified, or sold by such person as qualified for use in the transportation of hazardous materials.

D.6.3 Hazard Classification for GH₂ and LH₂

Compressed and liquefied hydrogen are designated as a hazard class, or division, of 2.1 (Flammable Gas) in 49 CFR 172.101 and 49 CFR 173.2.

Table D6.1 — Summary of hazard locations, conditions, and QD determination methods given in DoD 6055.9

Hazard Location	Hazardous Conditions	Method to Determine QD
Launch pad	 Two, or more, incompatible energetic liquids involved Proximity of fuel and oxidizer Frequency of launchings Lack of restraint of vehicle after liftoff Possibility of fallback with resultant dynamic mixing on impact 	Explosive equivalent, using the combined weight of the energetic liquids subject to mixing, applies
Static test stand	 Proximity of fuel and oxidizer, but test items are restrained and subject to better control than launch vehicles Two, or more, incompatible energetic liquids involved 	Explosive equivalent, using the combined weight of the energetic liquids subject to mixing, applies
Run tankage	 Direct feeding of fuel and oxidizer into an engine or device during operation Two, or more, incompatible energetic liquids involved 	Explosive equivalent, using the combined weight of the energetic liquids subject to mixing, applies; however, fire and fragment hazards govern if the run tanks meet the specified criteria
Ready storage	 Storage relatively close to launch and static test stand Does not directly feed engine as run tankage does Only one energetic liquid involved if facility design protects against fuel and oxidizer mixing, and against detonation propagation to other nearby areas 	Explosive equivalent, using the combined weight of the energetic liquids subject to mixing, applies; however, fire and fragment hazards govern if the facility design provides the required protection
Cold-flow test operation	 Only one energetic liquid involved The system is closed except for approved venting, is completely airtight, fuel and oxidizer never are employed concurrently, and each has a completely separate isolation system to preclude intermixing, and the energetic liquids are of required purity 	Fire and fragment hazards govern if the facility design provides the required protection; otherwise, explosive equivalent, using the combined weight of the energetic liquids subject to mixing, applies
Bulk storage	 Only one energetic liquid involved Most remote storage with respect to launch and test operations 	Fire and fragment hazards govern; except, in the special cases that are indicated
Rest storage	 Only one energetic liquid involved Temporary parking location for trailers, tank cars, barges, and portable holding tanks 	Fire and fragment hazards govern; except, in the special cases that are indicated
Pipeline	Only one energetic liquid involved.	Minimum 25-ft clear zone to inhabited buildings Energetic liquids that exhibit normal fire hazards (such as RP-1, JP-10, and Otto Fuel II) are excluded from this minimum distance Fire and fragment hazards govern as appropriate

Table D6.2 — Selection of federal regulations for hydrogen transportation

	Table D6.2 — Selection of federal regulations for hydrogen transportation					
49 CFR Part No.	Description					
General requirements for shipments and packaging						
171.8	Definitions and abbreviations					
172 Subpart G	Emergency response information					
172 Subpart H	Training					
173	Shippers — general requirements for shipments and packagings					
173.11	Shipper's registration statement; flammable cryogenic liquids					
173.31	Qualification, maintenance, and use of tank cars					
173.33	Hazardous materials in cargo tank motor vehicles					
173.34	Qualification, maintenance and use of cylinders (hydrogen-specific requirements listed)					
173.115	Class 2, Divisions 2.1, 2.2, & 2.3-Definitions (hydrogen is designated as 2.1)					
173.301	General requirements for shipment of compressed gases in cylinders (hydrogen-specific requirements listed)					
173.302	Charging of cylinders with nonliquefied compressed gases (hydrogen-specific requirements listed)					
173.314	Requirements for compressed gases in tank cars; (hydrogen-specific requirements listed)					
173.315	Compressed gases in cargo tanks and portable tanks					
173.316	Cryogenic liquids in cylinders (hydrogen-specific requirements listed)					
173.318	Cryogenic liquids in cargo tanks (hydrogen-specific requirements listed)					
173.319	Cryogenic liquids in tank cars (hydrogen-specific requirements listed)					
173.320	Cryogenic liquids; exceptions					
177.822	Acceptable articles					
177.823	Marking and placarding motor vehicles					
177.824	Retesting and inspection of cargo tanks					
177.826	Carrier's registration statement; flammable cryogenic liquids (includes Division 2.1 materials)					
180.407	Requirements for test and inspection of specification cargo tanks					
	Rail transportation					
172.101	Purpose and use of hazardous materials table (GH ₂ and LH ₂ are forbidden on passenger rail service)					
173.11	Shipper's registration statement; flammable cryogenic liquids					
173.31	Qualification, maintenance, and use of tank cars					
173.302	Charging of cylinders with nonliquefied compressed gases (hydrogen-specific requirements listed)					
173.314	Requirements for compressed gases in tank cars; (hydrogen-specific requirements listed)					
173.319	Cryogenic liquids in tank cars (hydrogen-specific requirements listed)					
174	Carriage by rail					
174.200	Special handling requirements (Division 2.1 materials)					
174.201	Class 2 (gases) material cylinders					
174.204	Tank car delivery of gases, including cryogenic liquids					
179	Specifications for tank cars					
179.10	Tank mounting					
179.13	Tank car capacity and gross weight limitation					
179.400	General specifications applicable to cryogenic liquid tank cars (includes DOT-113A60W					
	tank cars for transport of LH ₂)					
179.401	Individual specification requirements applicable to inner tanks for cryogenic liquid tank car tanks (hydrogen-specific requirements)					
179.500	Specification DOT-107A * * * * seamless steel tank car tanks					
179.500	Seamless steet talk cal talks					

Table D6.2 — Selection of federal regulations for hydrogen transportation (continued)

Aircraft transportation GH₂ forbidden on passenger aircraft. 150 kg max. permitted on cargo aircraft. LH₂ forbidden on passenger or cargo aircraft.	Table D6.2 — Sel	ection of federal regulations for hydrogen transportation (continued)			
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177.848 Segregation of hazardous materials		listed)			
	177.848	Segregation of hazardous materials			

Table D6.2 — Selection of federal regulations for hydrogen transportation (continued)

177.853	Transportation and delivery of shipments (includes Class 2 (gases) and Division 2.1
	materials)
177.859	Accidents; Class 2 (gases) materials (includes Division 2.1 materials)
178.57	Specification 4L; welded cylinders insulated (LH ₂ may be shipped in a DOT-4L cylinder)
178.345	General design and construction requirements applicable to Specification DOT 406
	(§178.346) cargo tank motor vehicles
	Packagings
178.3	Marking of packagings
178.37	Specification 3AA; seamless steel cylinders made of definitely prescribed steels or
	3AAAX; seamless steel cylinders made of definitely prescribed steels of capacity of over
	1,000 pounds water volume
178.57	Specification 4L; welded cylinders insulated (LH ₂ may be shipped in a DOT-4L cylinder)
178.320	General requirements applicable to all DOT specification cargo tank motor vehicles
178.337	Specification MC 331; cargo tank motor vehicle primarily for transportation of compressed
	gases as defined in Subpart G of Part 173 of this subchapter (Subchapter C – Hydrogen
	Materials Regulations)
178.338	Specification MC-338; insulated cargo tank
178	Appendix A - Specifications for steel
178	Appendix B - Alternative leakproofness test methods
180	Continuing qualification and maintenance of packagings



Annex E Relief Devices (Informative)

E.1 General

The following nomenclature is used in discussing relief devices.

operating pressure

The pressure at which a piping system is to be used on a steady-state basis. It may range from a vacuum to the design pressure. Special consideration should be given to the relief device choice to prevent simmer (preopening leakage) if a pressure higher than 90% of design is used.

set pressure

The pressure at which a protective device is set to discharge.

maximum allowable working pressure (MAWP)

The maximum pressure permissible at the top of a vessel in its normal operating position at the coincident operating temperature. It is the least of the values found based on calculations for every element of the vessel using nominal thickness exclusive of any allowances for corrosion or loadings other than pressure, and adjusted for any difference for static head that may exist between the part considered and the top of the vessel.

design pressure

The pressure used in the design of a vessel for the purpose of determining the minimum required thickness of the components of the vessel. When applicable, static head shall be added to the design pressure.

protective device

A generic term for any device designed to limit the pressure in a piping system.

safety device

An automatic protective device actuated by the static pressure upstream of the device and characterized by full opening pop action.

relief device

An automatic, reseatable protective device actuated by the static pressure upstream of the device and for which the opening is proportional to the increase in pressure over the opening pressure.

safety relief device

A protective device combining the functions of a safety device and relief device, usually being proportional during the first part of its stroke and having pop action during the last part.

system relief device

A protective device designed to the system pressure. This device should be set at or below the design pressure and should prevent the pressure from rising more than 10% above the design pressure.

isolation protective device

A protective device required on each isolatable piping section not directly connected to any external pressure source and for which the only pressure source when isolated is the nominal heat leak into the line. It should be set to open on a pressure no greater than 125% of the design pressure or 85% of the test pressure, whichever is lower. It should be sized to prevent the pressure from rising no more than 10% above these limits.

supplemental protective device

A protective device installed to protect against excessive pressure from abnormal sources or conditions. This device should be capable of preventing the pressure from rising above the test pressure. Its set pressure should not exceed 85% of the test pressure. It may be a safety or relief device.

Pressure-relief devices should be applied to all systems having a pressure source that can exceed the maximum allowable pressure of the system or for which the malfunction or failure of any component can cause the maximum allowable pressure to be exceeded. Relief devices are required downstream of all regulating valves and orifices unless the downstream system is designed to accept full source pressure. The protection provided by the ground pressurization system should be considered satisfactory when spacecraft operational or weight limitations preclude the use of relief valves and the systems operate in an environment not hazardous to personnel (unmanned spacecraft) only if that protection cannot be isolated from the spacecraft.

All pressure-relief devices should be sized and tested in accordance with the capacities of the pressure source and provide initial relief at the MAWP, or lower, in accordance with ASME BPVC.

Shutoff valves for maintenance purposes on the inlet side of a pressure-relief valve may be used if a means for monitoring and bleeding trapped pressure is provided. It is mandatory that the valve be locked open when the system is repressurized.

Hydrostatic testing systems for vessels not designed to sustain negative internal pressure should be equipped with fail-safe devices for relieving hazardous negative pressure during fluid removal. Thin-walled vessels that could be collapsed by a combination of events causing negative pressure should have negative pressure relief or prevention devices for safety during empty storage and transportation.

LH₂ vessels and each section of LH₂ piping capable of being isolated must be considered to be a pressure vessel with a source of external energy. This energy, for which the source is the heat leak into the line, can cause the pressure to increase many orders of magnitude as the fluid in the line heats to atmospheric temperature. Each such section must be equipped with a protective device for overpressure control.

Vacuum spaces shall have overpressure protection.

Insulated lines should be considered to be intact for sizing primary devices and catastrophically failed for sizing supplemental devices in designing relief systems. Insulation failures in LH₂ systems can cause air condensation and an increased heat flux into the system.

The following guidelines should be followed when evaluating devices against excessive pressures.

- The necessary amount to be blown off should be distributed if several safety devices are used so the remaining devices can blow off at least 75% of the total amount required if the largest safety device should fail.
- Two independent sources of energy should be available energy pipelines and driving mechanisms.
 If the pressure of the medium to be safeguarded serves for the drive, this is sufficient as one source of energy.
- The interval between start of excess pressure and full opening of the safety device should not be more than 5 s.

Safety valves should be unloadable and liftable. The force exerted by springs or weights should be reducible by hand operation from outside.

The pipelines and safety valves should be secured, taking into account local working conditions, so the static dynamic stresses (reaction forces) occurring with the quickest opening and closing can be taken up safely. All cross sections and pipelines should be designed to ensure the necessary discharge and undisturbed functioning of the safety valve. The material of all parts stressed by hydrogen during operations and testing should be suitable for the temperature and pressure conditions arising.

Pressure-relief systems should protect against a pressure regulator sticking or failing in the fully open position.

The maximum internal pressure and temperature allowed shall include considerations for occasional loads and transients of pressure and temperature. Variations in pressure and temperature may occur; therefore the piping system, except as limited by component standards or by manufacturers of components, shall be considered safe for occasional, short operating periods at higher than design pressure or temperature. Occasional variations above design conditions shall remain within the limits for pressure design as specified in ASME B31.3 paragraph 302.2.4 or ASME B31.1 paragraph 102.2.4, as appropriate.

E.2 Rupture Disks

Rupture disks are safety devices against excess pressure. They are specially dimensioned bursting elements, destroyed or permanently deformed on response.

In contrast to safety valves, blowoff orifices remain open after the rupture disk bursts. A similarly tested bursting element needs to be mounted or an exchange device inserted for further operation of the vessel. The rupture disk needs to be directly connected with the pressure space to be protected and may not be shut off. A changeover valve or similarly controlled fitting (interlocking device) is permissible in front of the rupture disk if two rupture disks are present and one serves as a reserve, provided one of the two rupture disks is always positively connected to the pressure space. The reliability of the interlocking device should be confirmed.

A rupture disk can be connected in series with a safety valve if it is operationally appropriate and it is not necessary to reckon with a rapid pressure rise (response inertia of safety valves). It should be ensured by suitable measure that fragments from bursting elements do not make the safety valve ineffective and cannot restrict the outflow cross section. It is also necessary to avoid the possibility of counter pressure (leaky disk) building up in the space between the rupture disk and safety valve because this affects the response pressure level of the disk.

The strength properties of the material used for the bursting elements should exhibit the least possible dependence on the type of stress (static or distention), temperature, and duration of the stress (curve of creep dependent on time).

E.3 Capacity Rating of Relief Devices

Some suggested heat leaks into LH₂ and LN₂ piping, and estimates of the gas evolved are given in Table E1.

The method of determining the capacity rating of a cryogenic relief device is recommended in 29 CFR 1910.103.

The capacity rating of a cryogenic relief device may be determined by the following formulas:

$$h_0 = h_1 + \frac{V_1^2}{2gJ} \tag{E1}$$

$$W_c = A_{iS_1}V_1 \tag{E2}$$

$$K = \frac{W_a}{W_c}$$
 (E3)

where:

h₀ = enthalpy of fluid at valve inlet, when velocity is assumed to be zero (Btu/lb)

 h_1 = enthalpy of fluid at throat (Btu/lb)

 V_1 = velocity of fluid at throat (Btu/lb)

 W_c = calculated flow rate (lb/s)

 A_t = area of throat (ft²)

 $\varsigma_1 = \text{density of fluid at throat (lb/ft}^3)$

 W_a = measured flow rate (lb/s)

S = entropy (Btu/lb·°R)

2gJ = proportionality constant

$$2gJ = 2 \times \frac{32.2 \text{ lb} \cdot \text{ft}}{\text{lb} \cdot \text{s}^2} \times \frac{778 \text{ ft lb}}{\text{Btu}} = 501,032 \frac{\text{lb} \cdot \text{ft}^2}{\text{Btu} \cdot \text{s}^2}$$

The properties and characteristics of hydrogen exiting from a relief device may vary depending on the particular fluid regions of the liquid, vapor, or gas. The following are recommended solutions for the various fluid regions.

Region I: Subcooled Liquid

Isentropic expansion reaches the liquid line before establishing equality at sonic velocity in Region I. Solve Equation E1 in the following form:

$$V_1^2 \text{sat} = (h_0 - h_s) 2gJ$$
 (E4)

and solve Equation E2 using the saturation velocity, V₁sat, and the liquid saturation density.

Region II: Superheated Fluid

Isentropic expansion establishes equality before the fluid reaches either saturated fluid line in Region II. The ideal throat velocity is sonic velocity at the solution point. Use the related density to solve Equation E2.

Region III: Supersaturated Gas

The fluid is a supersaturated gas if the isentropic expansion reaches the saturated vapor line on the temperature-entropy diagram before equality is established, insufficient time is available, and too few nuclei are present for condensation. Its properties are determined in the following fashion:

• Evaluate at the saturation pressure Psat, 4/3 x Psat, and 5/3 x Psat for all physical properties, and generate equations of the following form for each property:

$$X = C_0 + C_1 P + C_2 P_2$$
 (E5)

- Continue the expansion, assuming entropy is constant, until Equation E1 is solved by using the extrapolated values of enthalpy and sonic velocity generated by the polynomials.
- Evaluate Equation E2 by using the extrapolated values of density and sonic velocity.

Table E3.1 — Considerations for relief devices in LN₂ and LH₂ pipelines

Nominal pipe size	External area of pipe	Heat leak per 100 ft (30.5 m) of pipe ^a (Btu/min)			Gas evo		00 ft (30.5 n min)	n) of pipe	
in. (cm)	(ft²/ft)	Natural		For	ced	Foi	rced	Nat	ural
		LN ₂	LH ₂	LN ₂	LH ₂	LN ₂	LH ₂	LN ₂	LH ₂
0.5 (1.3)	0.220	220	1280	990	2200	36	1270	160	2180
1 (2.5)	0.344	340	2000	1550	3440	55	1980	252	3400
2 (5.1)	0.622	620	3600	2800	6200	100	3560	450	6140
3 (7.6)	0.916	920	5340	4130	9200	149	5300	671	9100
4 (10.2)	1.178	1180	6840	5300	11800	191	6790	860	11700
6 (15.2)	1.725	1725	10000	7760	17250	279	9900	1255	17100
8 (20.3)	2.27	2270	13150	10200	22580	367	13000	1650	22400
10 (25.4)	2.77	2770	16050	12450	27700	449	15900	2020	27400
12 (30.5)	3.33	3330	19300	15000	33300	539	19100	2430	32900

^a Based on the following experimental heat flux values (Btu/min·ft²):

Region IV: Saturated Vapor

Use the method of Region III except start at *Psat* and evaluate the properties at constant entropy upward for 4/3 x *Psat* and 5/3 x *Psat* for the common cause in cryogenic systems of a relief device relieving a saturated vapor (Region IV). Again, extrapolate and solve Equation E1. A series of solutions of this type can be correlated against saturation pressure in the manner of Napier's formula for steam. The following formulas may be used for initial saturation pressures ranging from 207 kPa (30 psia) to two-thirds of the critical pressure:

Oxygen W = 0.0410 (AP)Nitrogen W = 0.0422 (AP)Hydrogen W = 0.0231 (AP)

where:

W = flow rate, lb/s

 $A = area, in^2$

P = pressure, psia

Extending these equations to higher pressures is not recommended because the saturation enthalpy is not constant and the true solution deviates too far from the average value shown.

E.4 Recommended Principles

The recommended principles for relieving pressure are listed as follows:

- Single Device
 - Set pressure ≤ design pressure (DP)
 - Maximum relieving pressure ≤1.2 DP
- Supplementary Device
 - Set pressure not specified
 - Maximum relieving pressure ≤1.33 DP and ≤ test pressure

¹⁰ liquid nitrogen (natural convection)

⁴⁵ liquid nitrogen (forced convection at 15 mph (24 km/h) wind)

¹⁰⁰ liquid hydrogen (forced convection at 15 mph (24 km/h) wind)

- Thermal Device
 - Set pressure ≤1.25 DP
 - Maximum relieving pressure ≤ test pressure



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Annex G Index

Α

Acceptance test, xx, 62, 92 Access control, 48 Accidents, xiv, 1, 7, 22, 25, 103, 181, 182, 212, Aerospace, xiv, 2, 22, 27, 29, 62, 165, 182, 219, 220, 221, 242, 246 Aerospace pressure vessels, 62 Aging, 15, 62 Annual review, 245 Asbestos, 30, 164 Attendant, xx, 88, 98, 106 Authority having jurisdiction, xviii, xx, 2, 6, 7, 8, 9, 10, 35, 36, 37, 43, 46, 49, 51, 52, 55, 56, 57, 58, 59, 60, 62, 67, 68, 71, 73, 77, 86, 87, 89, 90, 92, 93, 95, 96, 98, 100, 101, 103 Autoiaintion temperature, 13, 17, 119 Autoignition, xx, 13, 17, 119, 130, 134, 205

В

Barges, 92, 230
Barricades, xxii, 25, 50, 51, 194, 207, 213
Barriers, 8, 51, 59, 63
Blast wave, xxii, 20, 26, 50, 209, 210, 211, 212, 213, 214, 215, 216
BLEVE, xx, 24
Boiling point, xviii, 11, 13, 79, 110, 112, 116, 120, 130, 134, 154, 188, 205
Bonding, 41, 63, 66
brass, 164, 165, 166, 173
Breathing Air, 12, 206
Buddy system, xx, 60, 87, 207
Buildings, 42

C

Cell
test, 43, 44, 45, 49, 194
Certification, xx, 7, 9, 36, 37, 53, 98
CHEMTREC, 96, 98
Cleaning, 78, 87, 88, 89, 90, 98
Codes, 217, 218
Cold trap, 79, 89
Collision, 27
Combustion, xiii, xxi, 1, 11, 15, 16, 17, 18, 19, 21, 22, 25, 26, 41, 45, 51, 77, 83, 85, 116, 117, 118, 119, 143, 177, 178, 210, 211, 217, 242, 243, 245, 248

Compatibility, xiii, 1, 28, 30, 31, 82, 88, 164, 244, 247, 248 Components, xxii, xxiii, 1, 13, 14, 22, 23, 29, 35, 40, 41, 42, 44, 50, 53, 54, 56, 57, 58, 62, 63, 64, 65, 66, 70, 73, 75, 78, 79, 85, 88, 90, 176, 207, 217, 218, 219, 220, 235, 237 connections, 70, 243 fittings, 68, 165 flanges, 68, 71 joints, 63, 66, 67 Condensation air, 59, 236 Confined Spaces, xx, 77, 83, 87, 98, 105, 106 Connections transfer, 70, 71, 243 Contamination, xxii, 13, 47, 59, 61, 70, 75, 78, 79, 88, 89, 90, 94 Contraction thermal, 28, 33, 34, 64, 74, 163 Control interconnected systems, 78, 79 Control room inert gases, 45, 245 piping systems, 218, 220, 241, 242, 243 structure, 44 ventilation, 44, 45, 101, 131, 135, 205 Cool down, 64, 93, 192 Coupling V-band, 70 Cryogenics, xx, 8, 28, 29, 30, 33, 34, 53, 55, 57, 58, 60, 64, 65, 68, 69, 70, 72, 84, 87, 88, 90, 93, 95, 97, 101, 105, 164, 186, 206, 218, 219, 230, 232, 233, 237, 240, 247, 249

D

Decontamination, 89, 90 Deflagration, 18, 19, 21, 22, 23, 24, 51, 77, 78, 107, 137, 184, 210 Deluge systems, 51, 52, 53, 97 Density, 11, 14, 94, 112, 116, 117, 118, 119, 120, 121, 122, 124, 130, 134, 178, 186, 188, 190, 199, 200, 205, 238 Design specification, 69 specifications, 69 Detection, 82, 83, 178, 248 fire, 1, 9, 51, 55, 82, 85, 86, 107, 174, 248 hydrogen, 45, 55, 82, 84 Detonation, xxi, 18, 19, 20, 21, 22, 23, 24, 45, 51, 77, 107, 137, 141, 142, 182, 183, 184, 210, 217, 220

limits, xxi pressure, 23 Diaphragm, 24, 45 Diffusion coefficient, 13 Dispersion, 51, 201 Documentation, xxiii, 7, 36, 53, 87 DOT, xviii, 58, 59, 95, 103, 132, 217, 229, 234	Fire, xviii, 24, 35, 51, 53, 55, 56, 98, 103, 104, 130, 132, 134, 205, 246, 247, 248, 249 detection, 248 extinguishing systems, 51, 53, 78 protection, xviii, 35, 246, 247 suppression, 52, 82, 100, 104 First aid training, 7, 37, 87, 96, 101, 105, 203, 232
E	Fittings, 68, 165, 166, 167, 237 Flame
Electric charge, 14, 15 Electrical equipment, 246, 247 Embrittlement, 31, 243, 244 low-temperature, 33, 59 reaction, 31, 33 Emergency plans, 100 response, 96, 101, 104, 105, 223	temperatures, 8 velocity, 21 Flame color, 16 Flammability, xiii, xv, xviii, xix, xxi, 15, 18, 19, 22, 24, 40, 107, 119, 137, 138, 139, 144, 184, 205, 242, 244, 245, 246, 248 lower flammability limit, 18 air, 141, 142, 244 halocarbon inhibitors, 139 pressure, xxi, 17, 18, 21, 64
security, 103 Emergency procedures, 1, 7, 36, 37, 204, 205, 207 cylinder fires, 102 spills hydrogen, 102	temperature, 18 upper flammability limit, 18 air, 141, 142, 244 halocarbon inhibitors, 139 pressure, xxi, 17, 18, 21, 64 temperature, 18
Emergency Procedures incident command system, xviii, 101 incident management system, 100, 247 training, 7, 37, 87, 96, 101, 105, 203, 232 Environmental, 31, 171	Flammable liquid, xxi, 47, 51 Flanges, 24, 29, 54, 61, 62, 63, 67, 68, 70, 71, 72, 73, 82, 87, 88, 93, 155, 156, 165, 181, 199, 219, 220 Flare systems, 75, 196
Evaporation, 13, 14, 24, 25, 51, 59, 79, 130, 134, 188, 196	Flow tests, 63
Examinations, 56 Exclusion area, xxi, 41, 44, 48, 103 Exhaust, 23, 25, 41, 49, 53, 77, 80, 83, 181	velocities, 15, 69, 189 Frostbite, 13, 22
Expansion, xiii, xx, xxii, 12, 13, 20, 34, 61, 62, 63, 64, 65, 68, 69, 71, 125, 162, 170, 186, 213, 238	G
Explosion prevention, 246 proof, 24, 39, 42 Explosive yields, 213 Exposure, xiv, 8, 12, 16, 26, 27, 28, 30, 31, 33, 46, 52, 64, 74, 83, 84, 88, 99, 105, 140, 145, 148, 150, 173, 204, 206, 221	Gaseous hydrogen system venting, 44, 46 Gaskets, 71, 72, 165, 181 Gloves, 90, 105, 206 Grounding, 39, 40, 60, 63 Guidelines, i, xvii, 1, 6, 7, 9, 10, 28, 35, 37, 39, 43, 45, 46, 47, 48, 49, 51, 57, 58, 87, 95, 96, 97, 204, 207, 216, 218, 221, 236, 242
F	Hazard chemical, xiii, 7, 11, 87, 116, 117, 118, 119 class, 95
Facility design, 1, 36, 37, 90, 216 Fail modes, 75 Failure modes and effects analysis, 37 Filter, 60, 61, 78, 88, 89	physical, 7, 87 Helium, xiv, 15, 19, 25, 31, 43, 61, 69, 76, 77, 79, 80, 84, 90, 91, 92, 173, 178, 188, 189, 199, 200

BSR/AIAA G-095-2004

Hoses, flexible, 68, 71, 89, 165 Hydrogen air mixture, 141, 142, 244 environmental, 31, 171 internal, 31, 41, 116, 117, 118, 120, 171 LH₂ spills, 12, 27, 102, 103 transfer, 88, 90, 92, 190, 192 normal, xiii, 11, 15, 109, 113, 120, 188 solid, 241 Hydrostatic test, xxii

ı

Ignition, 17, 21, 23, 24, 25, 40, 51, 59, 143, 157, 181, 204, 205, 206, 242, 247
Illumination, 42
Incident command system, xviii, 101
Incident management system, 100, 247
Instrumentation, 54, 55, 61, 62
Insulation
failure, 65, 75, 196
Isolation valve, 37, 45, 97

J

Joints expansion, xxii, 64, 65, 69 silver braze, 67

L

Labeling, 54 Leaks, 14, 15, 24, 25, 40, 45, 50, 55, 57, 59, 60, 61, 64, 69, 71, 75, 77, 80, 82, 83, 84, 87, 88, 90, 91, 92, 98, 101, 102, 178, 181, 185, 187, 188, 189, 190, 192, 193, 196, 197, 202, 207, 210, 235, 236, 239, 248 Loads earthquake, 62, 64 operating pressure, 56, 69, 70, 71, 73, 74 shock, xx, xxi, 20, 43, 62, 64, 143, 183, 209, 211, 215, 216 temperature, xiii, xx, xxi, xxii, 11, 13, 14, 15, 16, 17, 18, 19, 21, 22, 23, 25, 28, 29, 30, 31, 32, 33, 34, 52, 53, 54, 55, 56, 57, 58, 60, 61, 62, 63, 64, 70, 71, 73, 74, 75, 80, 83, 84, 85, 86, 88, 89, 92, 93, 99, 102, 109, 116, 119, 120, 124, 138, 139, 159, 160, 161, 162, 163, 164, 168, 169, 170, 171, 179, 183, 184, 185, 186, 188, 198, 201, 205, 219, 220, 235, 236, 237

vibration, 62, 64, 71, 143 weight, xxii, 16, 27, 57, 62, 64, 80, 89, 94, 209, 211, 212, 232, 236 wind, 24, 52, 62, 64, 75, 83, 98, 215, 239

M

Materials
general, 28
metallic, 28
nonmetallic, 29
welds, 29, 67
Mechanical properties
low temperatures, 11, 25, 30, 31, 32, 33, 59

N

Nonpropellant, xiii, 1, 2, 6, 45, 46, 59, 148, 150, 217, 220 Nonpropellant use, 194

0

Off-gassing, 22, 181
Operating procedures, 204
personnel, 7, 26, 41, 48, 49, 57, 87, 90, 96, 102, 105, 106, 143, 204, 206
Operational readiness review, 36
Operational Readiness Review, 36
Organic cleaning solvent, 89
O-rings, 29, 70, 71, 72, 92, 165
Overpressure, xxii, 72, 76
Oxygen
depletion, 105
storage, 150

P

Packaging, 95, 96, 230, 232
Personnel, 7, 26, 41, 48, 49, 57, 87, 90, 96, 102, 105, 106, 143, 204, 206 training, 204
Physiological, 26
Piping, 135 bending and forming, 65 GH₂, 64 LH₂ and SLH₂, 64 supports, 65
Pneumatic test, xxiii, 56
Police department, 99, 103 tanks, 95, 230, 232, 233

Pressure relief device, xxiii, 72, 73, 74, 236 rise, 14, 59, 65, 91, 99, 183, 185, 186, 188,	S
215, 237 supplemental relief, 74, 75 vessel, xxii, xxiii, 2, 6, 30, 35, 50, 53, 56, 57, 58, 62, 63, 95, 181, 211, 212, 217, 219, 220,	Safety assessment review, 37 communication, 87 devices, 236, 237
236 Pressure relief valve, xxiii, 194 Procedures	factor, 30, 36, 66, 196, 212 Schedule, 57, 190 Security, 100, 104
cleaning, 89 cool down, 64, 93, 192 operating, 22, 87, 97, 204, 207	Set pressure, 73, 74, 196, 235 Shipping, 95, 96, 132 Shock, xx, xxi, 20, 43, 62, 64, 143, 183, 209,
purging, 59 Propellant use, 194 Propellants, xxii, 1, 6, 7, 45, 46, 47, 48, 49, 59,	211, 215, 216 Shoes, 90, 105, 206 Shutoff valves, 29, 59, 70, 72, 78
210, 212, 214, 216, 217, 221 Properties LH ₂	Slush, xix, 6, 248 Solubility, helium, 15 Spark generation, 41
density, 14 SLH ₂ aging, 15	Spills, LH ₂ , 12, 27, 102, 103 Standard, xx, xxi, xxiii, 29, 47, 67, 68, 69, 87, 97, 165, 201, 217, 220, 221, 222 Storage
vapor pressure, 130 Protection, xviii, 35, 50, 131, 135, 246, 247 fire, xviii, 35, 246, 247 Pumps	LH ₂ liquid propellant, 46 nonpropellant use, 45 tanks, 69
vacuum, 61, 79, 80 Purging, 25, 88, 91, 181, 199	Stratified flow, 65, 93 Supplemental pressure relief, 74 Supports, 62, 64 Surface film, 31
Quantity-distance guidelines criteria, 46	Т
quantity-distance tables, 59 Quenching distance, 17, 42	Tagging, 53 Tank
Quenching gap, xxiii	pressure, 211 Temperature, xviii, xx, 116, 117, 119, 120, 121, 122, 125, 130, 134, 139, 163, 168, 169, 170, 179, 205, 245
Radiation, energy, 12, 14, 16, 26, 27, 45, 52, 59, 61, 76, 77, 85, 86, 139, 140, 179, 212, 220 Railroad cars, 92 Records, 57 Redundancy, 8	Test/Testing, xviii, xx, xxii, xxiii, 6, 9, 28, 30, 33, 36, 40, 41, 42, 43, 44, 45, 48, 49, 50, 54, 56, 57, 60, 61, 62, 63, 68, 69, 70, 71, 74, 84, 86, 92, 93, 98, 102, 168, 171, 189, 194, 216, 217, 219, 232, 235, 240, 242, 243, 244, 248 system, 69
Relief valves, xxiii, 60, 70, 73, 74, 76, 78, 79, 92, 101, 186, 194, 195, 196, 236	Thermal cycling, 33, 61, 92, 207 expansion, 12, 34, 61, 62, 64, 65, 68, 170, 186 radiation, 12, 16, 27, 45, 77, 139, 140, 220 Tools sparkproof, 206
	Toxicity, 28 transfer

BSR/AIAA G-095-2004

connections, 70, 71 LH₂, 92 Transfer connections, 70 Transport, 27, 63, 92, 95, 96, 97, 229, 232, 233 Transportation, i, xiv, xv, 1, 8, 27, 92, 95, 96, 97, 98, 212, 217, 229, 230, 232, 233, 234, 236 public thoroughfare emergency response, 96 training, 7, 37, 87, 96, 101, 105, 203, 232 public thoroughfares noncommercial, 96

U

Unit conversion, 7 Upward flame propagation, 18

V

Vacuum systems, 53, 64, 79
Valves, xxii, 14, 23, 24, 25, 29, 37, 44, 45, 49, 54, 59, 60, 61, 62, 63, 70, 73, 74, 76, 78, 79, 82, 92, 101, 165, 206, 219, 220, 235, 236, 237
Vapor cloud, 102, 211, 212 pressure, 130 travel, 50, 51

Vaporization, xx, 8, 15, 20, 24, 25, 51, 60, 102, 103, 116, 117, 120, 157, 189, 190, 192 V-band couplings, 70 Velocity flame, 21 flow, 15, 69, 189 stack, 23, 25, 40, 47, 49, 53, 58, 75, 76, 98 Vent and exhaust, 181 Vent/Venting, 75, 98, 107, 151, 199, 246 deflagration, xiv, xxi, 19, 77, 184, 205 Ventilation, 44, 45, 101, 131, 135, 205 Vessel aerospace pressure, 62 design, 97 mobile, 60, 98 support, 62

W

Waivers, 10
Warning systems, 9, 76
Water spray systems, 51, 52
Welding, xxv, 22, 23, 29, 32, 41, 42, 47, 56, 63, 66, 67, 71, 85, 143, 148, 150, 217, 218, 220, 242, 246